I. EFFORTS TOWARD THE SYNTHESIS OF ALIPHATIC IODONIUM SALTS

II. FLUORINE-19 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF CYCLIC AND BICYCLIC SYSTEMS

Thesis by

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To my dear parents

The chymists are a strange class of mortals impelled by an almost insane impulse to seek their pleasure among smoke and vapor, soot and flame, poisons and poverty, yet among all these evils I seem to live so sweetly, that may I die if I would change places with the Persian king.

-Becher-

ACKNOWLEDGMENTS

Graduate school is truly a rewarding and a humbling experience that well succeeds in making one feel, in the words of the great Newton, like a mere pebble on the beach whilst a great ocean of truth lies before one. Among those who have made my graduate career rewarding is Professor John D. Roberts; from Professor Roberts I hope that I have acquired in some small measure the confidence to independently pursue original research.

Professors George S. Hammond and Harry B. Gray have affected significantly my graduate residence. Their zeal and eloquence in introducing new changes in chemical education has been most infectious. These gentlemen also provided many interesting if not always challenging hours of amusement on the links and in the billiard room, respectively.

One learns most from his peers; from Dr. Dennis J. Diestler and Dr. Frank J. Weigert I have learned much. Jim Magnuson, Rudolf Knorr, Remon Hagen, Ruth Lack, Duncan Hunter, Klaus Grohmann and Manfred Jautelat have also helped make life in the Roberts group worthwhile in many respects.

To the secretarial staff, and in particular to Birgitta Isaacson, are due many thanks for assistance over the years. This thesis would probably not have been completed without the expert typing of Mrs. Edi Bierce and Mrs. Rita Baldwin.

Finally, thanks are due the Department of Chemistry for its generous financial assistance: for graduate teaching assistantships during the period 1963-1968, for a graduate research assistantship during the year 1967-1968, and for receipt of the DuPont Teaching Award, also during the year 1967-1968.

In the writing of this thesis I have attempted to adhere to the guidelines laid down in W. Strunk, Jr. and E. B. White, "The Elements of Style," L. F. Fieser and M. Fieser, "Style Guide for Chemists," and the American Chemical Society publication "Handbook for Authors." Whenever an occasional disagreement arose between these authorities, the dilemma was promptly resolved by quick use of a five-cent coin.

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II. FLUORINE-19 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF CYCLIC AND BICYCLIC SYSTEMS

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ABSTRACT

The synthesis of iodonium salts of the general formula $[C_6H_5IR]^+X^-$, where R is an alkyl group and X^- is a stabilizing anion, was attempted. For the choice of R three groups were selected, whose derivatives are known to be sluggish in S_N1 and S_N2 substitutions: cyclopropyl, 7,7-dimethyl-1-norbornyl, and 9-triptycyl. The synthetic routes followed along classical lines which have been exploited in recent years by Beringer and students. Ultimately, the object of the present study was to study the reactions of the above salts with nucleophiles. In none of the three cases, however, was it possible to isolate a stable salt. A thermodynamic argument suggests that this must be due to kinetic instability rather than thermodynamic instability. Only iodocyclopropane and 1-iodoapocamphane formed isolable iododichlorides.

Several methylated 2,2-difluoronorbornanes were prepared with the intent of correlating fluorine-19 chemical shifts with geometric features in a rigid system. The effect of a methyl group on the shielding of a β-fluorine is dependent upon the dihedral angle; the maximum effect (an upfield shift of the resonance) occurs at 0° and 180°, whereas almost no effect is felt at a dihedral angle of 120°. The effect of a methyl group on a γ-fluorine is to strongly shift the resonance downfield when fluorine and methyl group are in a 1,3-diaxial-like relationship. Molecular orbital calculations of fluorine shielding in a variety of molecules were carried out using the formalism developed by Pople; the results are, at best, in modest agreement with experiment.

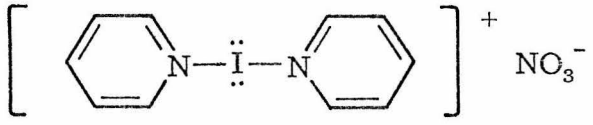
EFFORTS TOWARD THE SYNTHESIS OF ALIPHATIC IODONIUM SALTS

EFFORTS TOWARD THE SYNTHESIS OF ALIPHATIC IODONIUM SALTS

I. Background and Introduction

The ability of iodine to form compounds with coordination number greater than one is well known, common examples being the interhalogen compounds ICl_3, IF_5, and the anion I_5^-. In general, compounds in which the iodine has a coordination number greater than two are those in which the ligands are very electronegative groups, in which case we may conveniently assign a positive oxidation number to the iodine, or in which the iodine is definitely known to be in a positive oxidation state. Common oxidation numbers for electropositive iodine are +1 and +3. Data from nuclear quadrupole spectroscopy have been adduced in favor of the electropositive nature of iodine in ICN and ICl (1), whereas I^{3+} ions stabilized by coordination almost certainly exist in solutions of $I(OCOCH_3)_3$ or IPO_4.

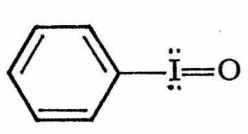
Positive organoiodine compounds are also very common. The unipositive iodine compound Ipy_2NO_3 is best formulated as $[\,py\text{-}I\text{-}py\,]^+NO_3^-$(I) since an acetone solution of it is moderately conducting.



(I)

Recent spectroscopic evidence suggests that the iododipyridinium ion has a linear N–I–N structure (2).

Positive tricoordinate iodine occurs in iodosobenzene (II), iodobenzene dichloride (III) and diphenyliodonium iodide (IV).



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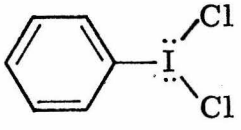

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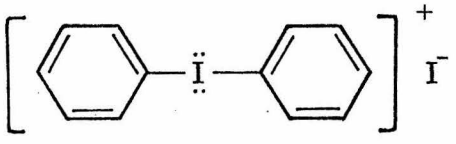
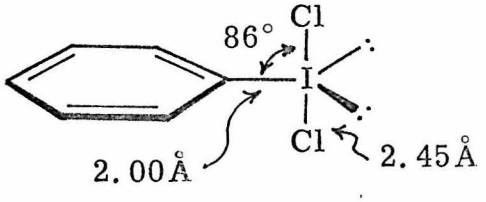


(IV)

Iodobenzene dichloride (V) is formulated as having a decet of electrons about the iodine, consistent with the observation that the ICl_2 group is linear, symmetrical and at approximately right angle to the plane of the benzene ring (3).



(V)

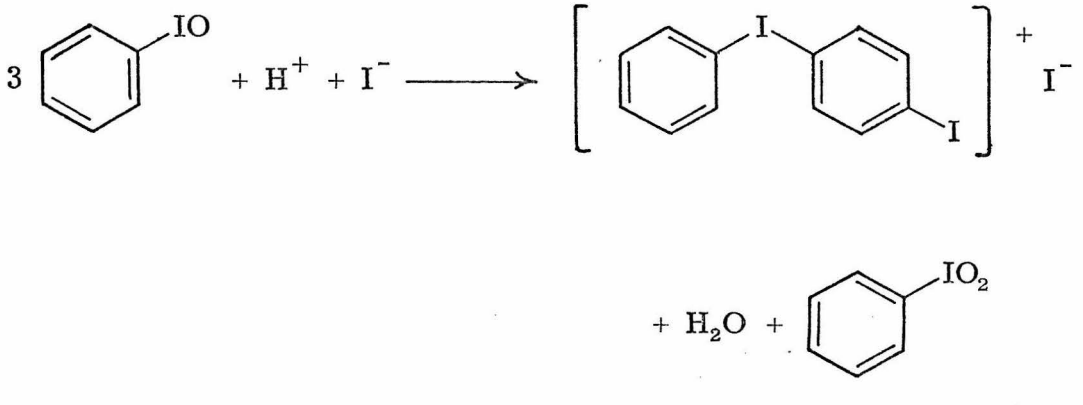
In order to accommodate ten electrons the valence shell of iodine must expand; a hybridization scheme which is consistent with the observed trigonal bipyramidal structure is dsp^3 hybridization. Pauling estimates that the pure single-bond iodine radius is 1.363 Å (4).

Combining this with the single-bond carbon radius of 0.77 Å and noting that no electronegativity correction has to be made, one arrives at a value of 2.133 Å for a pure single-bond C–I length. The experimental value of 2.00 Å, indicated in the diagram above, suggests partial double-bond character.

Since the structure of diphenyliodonium iodide is formulated with an octet of electrons about the iodine, it is likely that the hybrization is approximately tetrahedral (sp^3). In the more ionic salt, diphenyliodonium fluoroborate, the C–I–C bond angle is 94° and the C–I bond length is 2.03 Å (5).

As far as the chemistry of organoiodine compounds is concerned, that of the diaryliodonium compounds has been the most extensively explored. These salts were first discovered nearly 75 years ago by the ubiquitous Victor Meyer. He reported that when iodosobenzene is treated with concentrated sulfuric acid and then with aqueous potassium iodide, a salt is obtained, mp 144°, having the formula $C_{12}H_9I_3$ (6).

This compound is probably p-iododiphenyliodonium iodide.



The fate of the iodoso oxygen was not determined; the equation above gives one plausible explanation. Upon solid distillation, p-iododiphenyliodonium iodide yields iodobenzene and p-diiodobenzene. This general reaction was often used as a structure proof of the salts.

In the years that followed Meyer's initial discovery other salts were prepared and studied by Meyer and his students, by Willgerodt, and by others. The entire field of polyvalent organoiodine chemistry has been reviewed about once every 25 years (7, 8, 9).

Methods of synthesis of diaryliodonium salts have included the following:

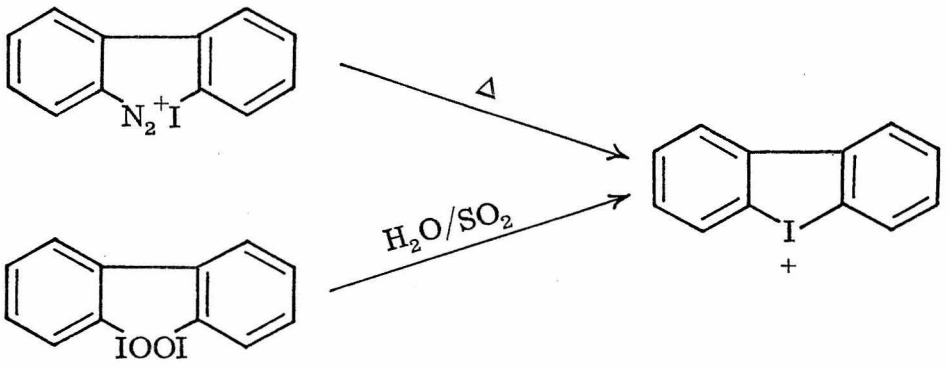
1) $ArIO + Ar'IO_2 \xrightarrow{OH^-} [ArIAr']^+IO_3^-$

2) $Ar_2Hg + Ar'ICl_2 \longrightarrow [ArIAr]_2^+SO_4^= + 2H_2O$

3) $4ArH + (IO)_2SO_4 \longrightarrow [ArIAr]_2^+SO_4^= + 2H_2O$

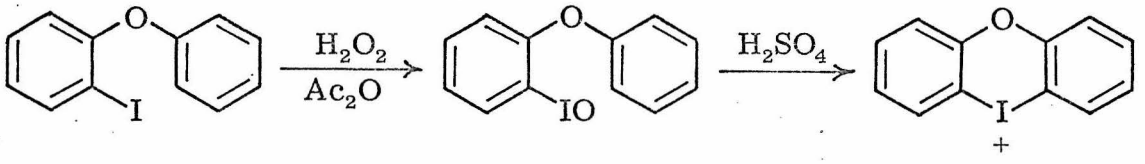
4) $ArIO + Ar'H \xrightarrow{HX} [ArIAr']^+X^- + H_2O$

By far it is the last method that is superior and it is this method which has been used by Beringer to prepare a whole family of iodonium compounds (10a, b). Method (3) is suitable but is limited to only symmetrical compounds (11a-d). The iodine was first incorporated into a cyclic system by Mascarelli who made the very interesting biphenyleneiodonium system (VI) from the azo precursor (12) and from the diiodoso derivative (13).

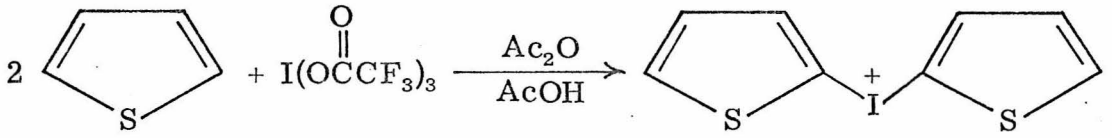


(VI)

Oxygen-, nitrogen- or sulfur-containing heterocyclic iodonium salts have been prepared by Beringer using standard methods (14).



Finally, diaryliodonium compounds are known in which the aromatic system is not benzenoid (15).



The most prominent reaction undergone by diaryliodonium compounds is their reaction with nucleophiles. In this respect, the diaryliodonium salts prove to be excellent phenylating agents. The flow diagram on the next page gives some idea of the scope of the reaction (16).

In contrast to the contentions of Lucas (17) and in contrast to any tempting similarities to the S_N1 behavior of aromatic diazonium compounds, the diaryliodonium compounds are very susceptible to S_N2-type mechanisms. In studying reaction 2 above, Lewis and Stout (18) found that the rate of decomposition is indeed dependent on hydroxide concentration, but they could not verify that the state of affairs is as simple as the following pair of consecutive bimolecular reactions:

$$(C_6H_5)_2I^+ + OH^- \xrightarrow{k_1} C_6H_5I + C_6H_5OH$$

$$(C_6H_5)_2\overset{+}{I} + C_6H_5O^- \xrightarrow{k_2} C_6H_5I + (C_6H_5)_2O\ .$$

Beringer studied reaction 3 in detail for the case where OR^- was phenoxide ion (19). He showed that the reaction is second order in most dioxane-water mixtures, but that it approaches first order as the dioxane concentration is increased. This, plus the fact that as the initial stoichiometric concentration of iodonium compound is increased, the second-order rate constant drifts downward, suggested that the reaction proceeds through ion-pairs.

$$Ar'_2I^+ + \bar{O}Ph \underset{}{\overset{K}{\rightleftharpoons}} Ar'_2\overset{+}{I}OPh \xrightarrow{k} Ar'OPh + Ar'I\ .$$

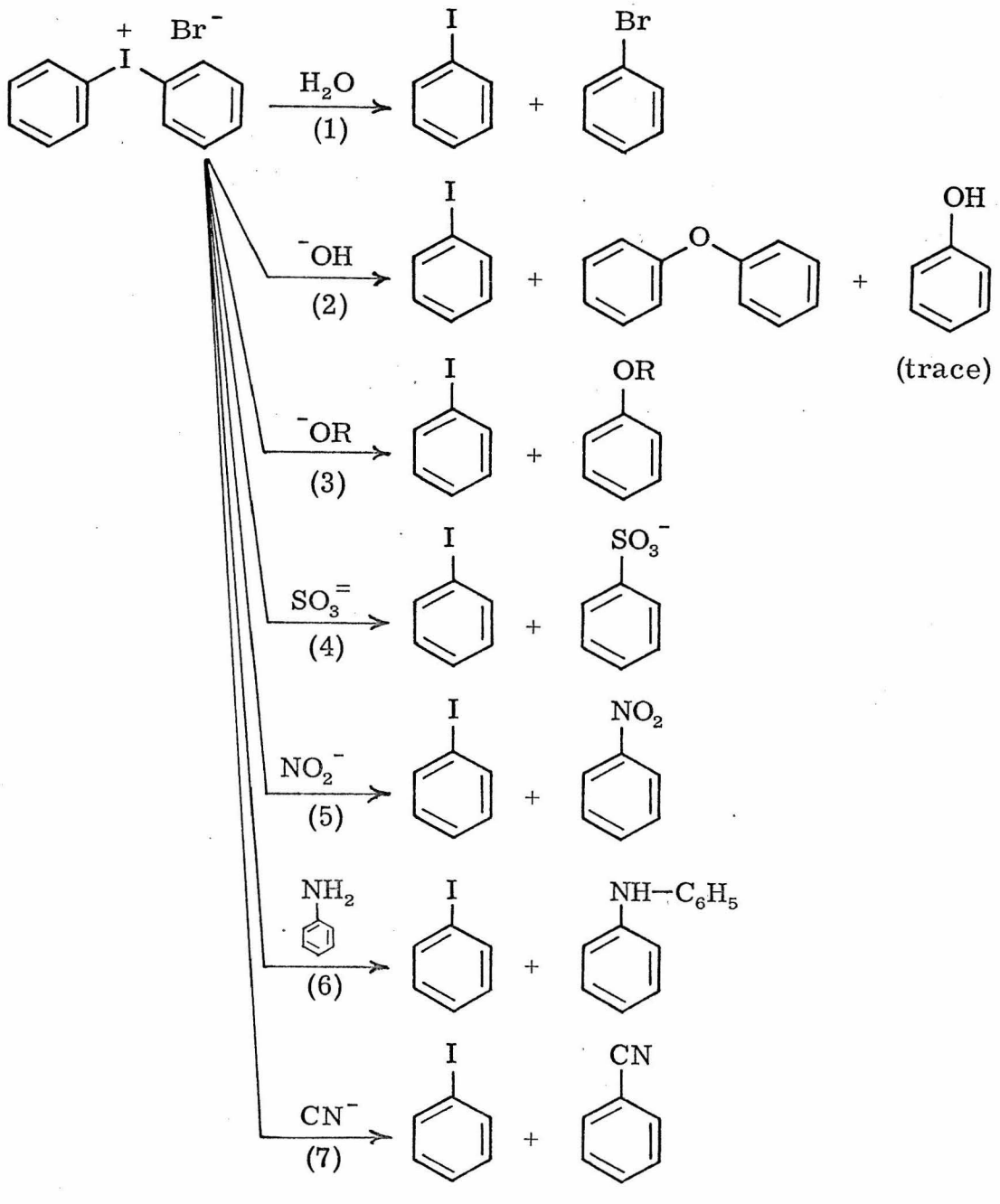
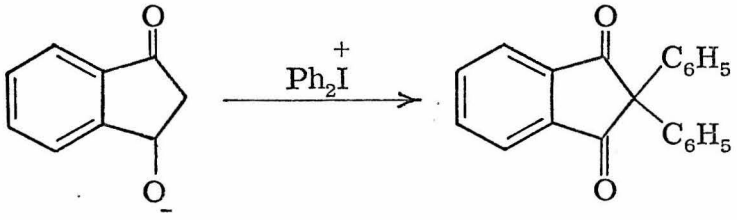


Figure 1. Reactions of diaryliodonium salts with nucleophiles

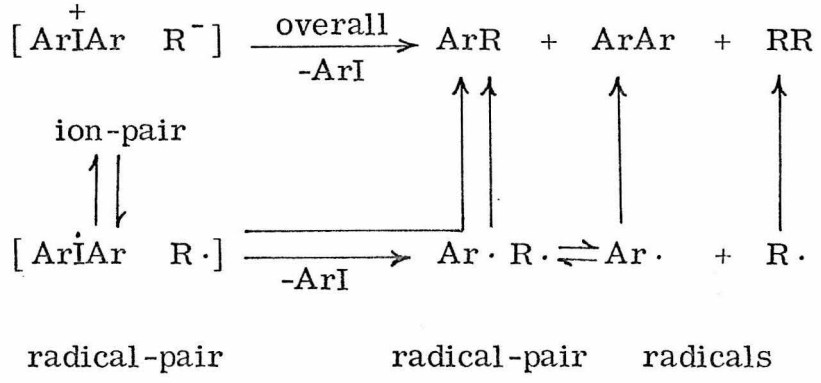
Additional kinetic experiments in the case of the decomposition of diphenyliodonium chloride to chlorobenzene and iodobenzene gave much support to the ion-pair hypothesis (20).

Different behavior is encountered when the attacking nucleophile is an anion of a 1,3-indandione. Here, Beringer found that 2-phenyl-1,3-indandione gives 2,2-diphenyl-1,3-indandione (VII), and that if this reaction be carried out in the presence of styrene, there results a decrease in yield and the appearance of low polymers of styrene (21). This suggested that the initial carbanion is oxidized to a radical that



(VII)

initiates polymerization. The tentative mechanism proposed by Beringer is shown below:



The reasonableness of diphenyliodine as an intermediate was supported by Beringer's earlier work on the polarographic reduction of iodonium salts (22), which showed that polarograms of diaryliodonium salts have three waves, probably corresponding to the following processes:

$$\overset{+}{\text{ArI}}\text{Ar} + e^- \rightleftharpoons \dot{\text{Ar}}\text{IAr}$$

$$\overset{+}{\text{ArI}}\text{Ar} + 2e^- + H^+ \longrightarrow \text{ArH} + \text{ArI}$$

$$\overset{+}{\text{ArI}}\text{Ar} + 4e^- + H^+ \longrightarrow \text{ArH} + \text{Ar}^- + I^-$$

Certain other chemistry of iodonium salts seems best explainable in terms of radical reactions. Thus, treatment of pyridine with diphenyliodonium chloride in the presence of sodium hydroxide produces α-, β-, and γ-phenylpyridines instead of N-phenylpyridinium chloride (23). This indicates that the normal directive influences of the pyridine nucleus are not in operation, and that a free-radical mechanism obtains:

$$[\,\text{PhIPh}\,]^+\text{OH}^- \rightleftharpoons \text{Ph–I(OH)–Ph}$$

$$\text{Ph–I(OH)–Ph} \longrightarrow \text{PhI} + \text{HO}\cdot + \text{Ph}\cdot$$

$$\text{Ph}\cdot + \text{C}_5\text{H}_5\text{N} \longrightarrow \alpha\text{-, } \beta\text{-, } \gamma\text{-isomers}$$

Reactions of diphenyliodonium chloride with mercury (24, 25) and with tellurium (26) may also be radical in nature.

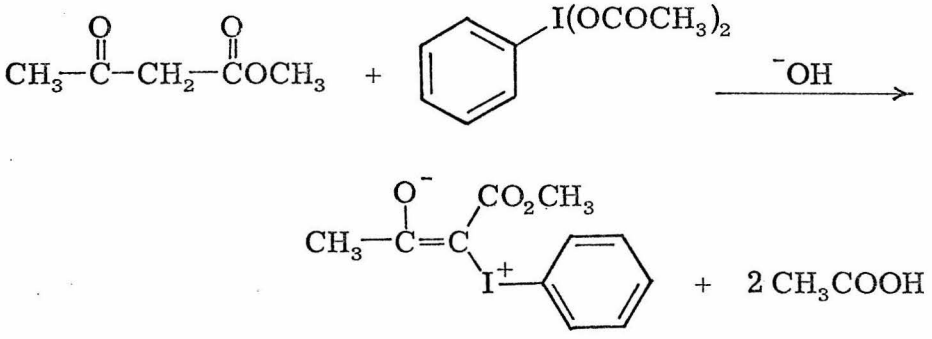
II. Statement of the Problem

The driving force for initiating the present work was derived from two sources:

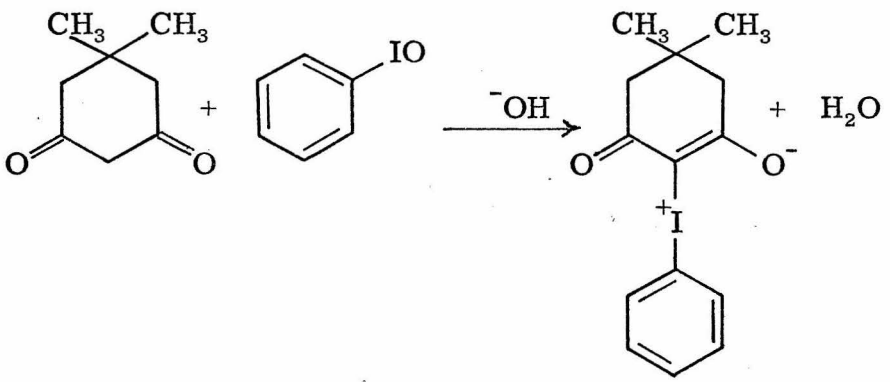
1) First, there was the observation that iodonium salts in which one or both of the ligands are saturated groups are unknown.

2) Second, certain data accumulated by Caserio, Glusker, and Roberts (27a, b) on the hydrolysis of unsymmetrical diaryliodonium salts appeared highly interesting and worthy of further examination.

One of the earliest attempts at the preparation of an aliphatic iodonium salt is that due to Lachman (28). He treated diethylzinc with iodobenzene dichloride, hoping to get ethylphenyliodonium chloride and ethylzinc chloride. Instead, a mixture of iodobenzene, ethyl chloride, zinc chloride and zinc oxychloride was obtained. Certain iodonium betaines (VIII, IX) have been prepared by Neilands and co-workers by the reaction of β-diketones with iodoso derivatives or iodosodiacetates in the presence of base (29, 30, 31, 32).



(VIII)

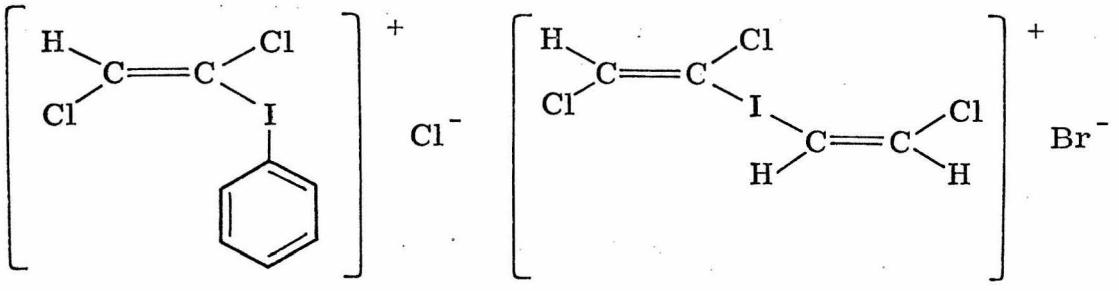


(IX)

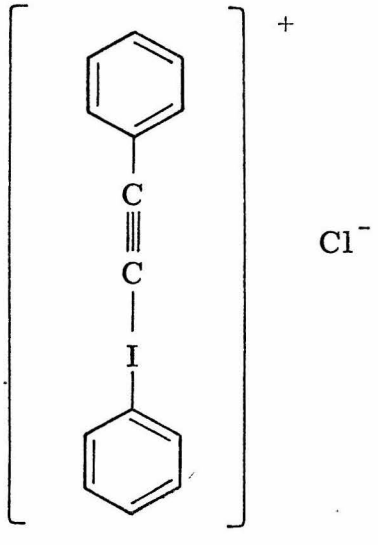
These crystalline substances are unstable but isolable materials.

Iodonium salts in which one or both of the ligands are ethylenic or acetylenic have been known for some time. Several salts of the type shown below (X, XI) were prepared around the turn of the century (33). More recently, Beringer has prepared (XII) by the reaction of lithium phenylacetylide with iodobenzene dichloride. On standing overnight at room temperature, iodonium salt (XII) decomposes (34). The salt, phenyl(α-chlorostyryl) iodonium fluoroborate, is stable at room temperature; this fact suggests that (XII) is unstable because it undergoes facile nucleophilic attack by the moderately nucleophilic chloride anion. This also provides a possible reason why compounds such as dimethyliodonium salts have never been prepared.

It seemed plausible that fairly stable aliphatic iodonium salts could be prepared if one or both of the ligands be groups that are known to be sluggish to nucleophilic attack. The cyclopropyl, 1-apocamphanyl, and 9-triptycyl groups offered themselves as potential



(X) (XI)



(XII)

Figure 2. Some isolable, unusual iodonium salts

candidates. Cyclopropyl derivatives are very unreactive by both S_N1 and S_N2 mechanisms (35), and the extreme inertness of 1-norbornyl and 9-triptycyl derivatives has been known for a long time (36).

It is possible to perform a crude thermodynamic calculation of the stability of an hypothetical aliphatic iodonium salt such as dimethyliodonium chloride. Figure 3 outlines the various processes that must be carried out in converting the elements to the crystalline salt. In Table 1 there are tabulated the enthalpies of these processes. All values are given in kcal; the associated references indicate the source of the data when this is known. The computed heat of formation from the indicated data is thus $258 + \Delta H_1 + \Delta H_2 + U$ kcal/mole. In order to

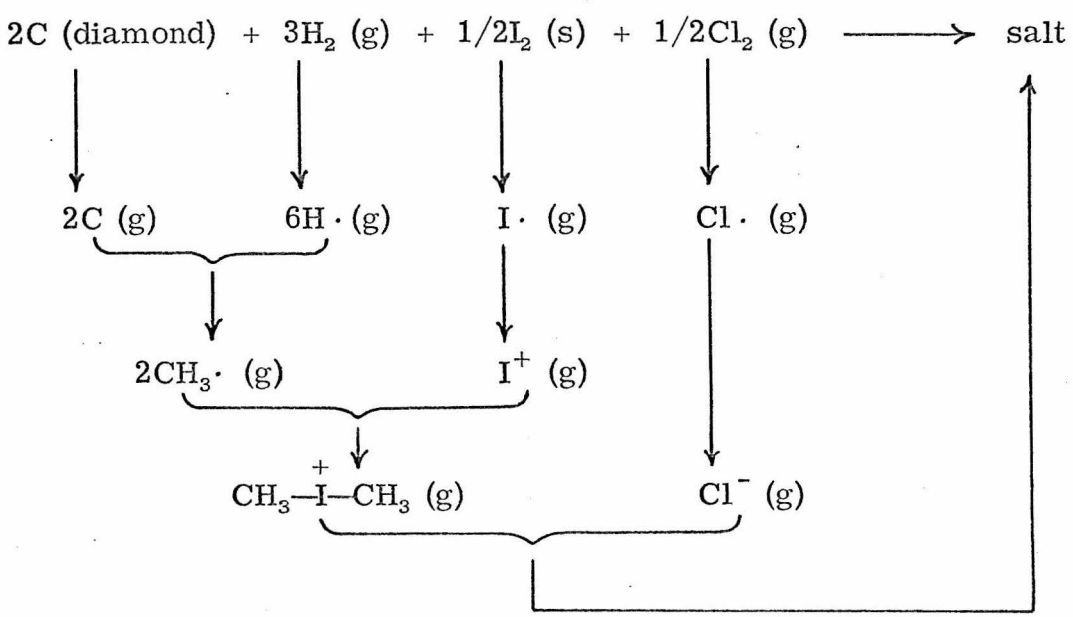


Figure 3. Born-Haber cycle used in stability calculation of dimethyliodonium chloride

Table 1. Thermodynamic Data for Formation of Dimethyliodonium Chloride

Process	ΔH	Ref.
1) $2C\ (diamond) \longrightarrow 2C\ (g)$	343	a
2) $3H_2\ (g) \longrightarrow 6H\cdot\ (g)$	313	b
3) $1/2\,I_2\ (s) \longrightarrow I\cdot\ (g)$	13	a
4) $I\cdot\ (g) \longrightarrow I^+\ (g) + e^-$	240	c
5) $1/2\,Cl_2\ (g) \longrightarrow Cl\cdot\ (g)$	29	b
6) $Cl\cdot\ (g) + e^- \longrightarrow Cl^-\ (g)$	-87	d
7) $2C\ (g) + 6H\cdot\ (g) \longrightarrow 2CH_3\cdot\ (g)$	-593	b
8) $CH_3\cdot\ (g) + I^+\ (g) \longrightarrow CH_3\text{–}I^+\ (g)$	ΔH_1	
9) $CH_3\text{–}I^+\ (g) + CH_3\cdot\ (g) \longrightarrow CH_3\text{–}I^+\text{–}CH_3\ (g)$	ΔH_2	
10) $CH_3\text{–}I^+\text{–}CH_3\ (g) + Cl^-\ (g) \longrightarrow [\,CH_3\text{–}I\text{–}CH_3\,]^+\,Cl^-\ (s)$	U	

[a] L. C. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, 1960, p. 86.

[b] L. C. Pauling, ibid., p. 85.

[c] C. E. Moore, "Atomic Energy Levels," Nat. Bur. Std. Circ. 467, Vol. 3, Washington, D.C., 1958, p. 105.

[d] L. C. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, 1960, p. 511.

estimate ΔH_1, we note that the bond dissociation energy of a bond A^+–B can be related to that of the bond A–B as follows:

$$\text{BDE } (A^+\text{–B}) = \text{BDE } (\text{A–B}) + \text{IP } (\text{A}) - \text{IP } (\text{A–B}). \qquad \text{(I-1)}$$

In the present case we have the equation

$$\text{BDE } (CH_3\text{–}I^+) = \text{BDE } (CH_3\text{–I}) + \text{IP } (\text{I}) - \text{IP } (CH_3\text{–I}). \qquad \text{(I-2)}$$

Taking 57 kcal as the carbon-iodine bond energy and 219 kcal as the ionization potential of methyl iodide (37), one computes ΔH_1 to be -78 kcal.

In a similar manner, the value of ΔH_2 can be derived from the equation

$$\text{BDE } (CH_3I^+\text{–}CH_3) = \text{BDE } (CH_3\text{I–}CH_3) + \text{IP } (CH_3) - \text{IP } (CH_3\text{I–}CH_3). \qquad \text{(I-3)}$$

The carbon-iodine bond energy in dimethyliodine is almost surely less than that in methyl iodine (57 kcal). Since the average iodine-chlorine bond energy in ICl_3 is approximately 7 kcal less than in ICl, a value of 50 kcal shall be adopted for the above. The ionization potential of dimethyliodine is also probably less than that of methyl iodide. Since in the sequence $CH_4 \rightarrow C_2H_6 \rightarrow (CH_3)_3CH \rightarrow C(CH_3)_4$ the ionization potentials decrease on the average by about 1 ev for each methyl substituent (38), a value of 196 kcal shall be adopted for $IP(CH_3I\text{–}CH_3)$. Taking a value of 226 kcal for the ionization potential of the methyl

radical (39), one computes ΔH_2 to be -80 kcal. Hence, the heat of formation of the iodonium salt is 100 + U kcal.

The lattice energy U is the most difficult term to evaluate. Kapustinskii has developed an approximate expression, applicable to all types of crystals and to situations where crystallographic data are lacking, for making lattice energy calculations (40).

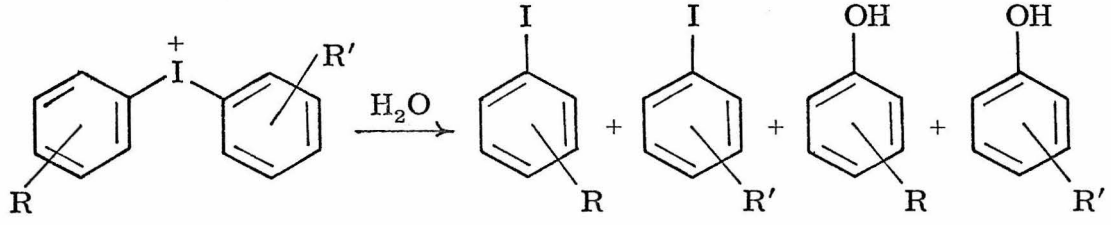
$$U = \frac{287.2 \nu Z_1 Z_2}{r_a + r_c}\left(1 - \frac{0.345}{r_a + r_c}\right) \qquad \text{(I-4)}$$

In this expression Nv is the number of ions in one gram-molecular weight of the substance, the Z's are the charges, and the r's are the anion and cation radii whose sum should, in principle, equal the experimental internuclear distance. For the present case we may take $r_a + r_c = 3.08$ Å, the value of the iodine-chlorine distance in diphenyliodonium chloride (5); this gives a value of -165 kcal for U. A correction for the fact that U is really an internal energy rather than an enthalpy will not be made since this is likely to be small (1-5 kcal). Likewise, corrections due to dispersion forces, zero-point energy of the crystal, electrical multipole effects, etc. will not be made. The calculated overall heat of formation is thus -65 kcal/mole.

Examination of tables of thermodynamic data (41) shows that entropies of formation of ionic chlorides generally fall in the range -20 to -70 cal/mole deg. A value for ΔS_f° of -70 cal/mole deg would give an overall free energy of formation of -44 kcal/mole.

This crude but convincing calculation served to strengthen the hope that it should be possible to prepare aliphatic iodonium salts, at least from the standpoint of thermodynamic stability. Naturally, it would not be possible to say very much about their kinetic stability.

The second reason for initiating work on the present project is purely mechanistic in nature. Caserio, Glusker, and Roberts showed that when unsymmetrical diaryliodonium salts possessing weakly nucleophilic anions (such as fluoride, tosylate, and fluoroborate) are hydrolyzed, the direction of cleavage is essentially insensitive to the nature of the substituents (27).



(XIII) (XIV) (XV) (XVI) (XVII)

Table 2 shows the distribution of iodides (XIV) and (XV) obtained for various substituents.

Table 2. Product Distribution in the Hydrolysis of $(C_6H_4R)\overset{+}{I}(C_6H_4R')X^-$

R	R′	X^-	Mole per cent (±5%)[a] (XIV)	(XV)
H	4-CH_3O	OTs^-	30-40	70-60
H	3-CH_3	OTs^-	43-46	57-54
3′-NO_2	4-CH_3O	OTs^-	47	53

[a] Determined by infrared spectroscopy on the mixture.

Similar insensitivity was shown toward the nature of the anion. The data above are not consistent with a polar mechanism, whether it be S_N1 in nature or S_N2 in nature. This, plus the fact that the hydrolyses are catalyzed by copper [either Cu(I) or Cu(II)], led the authors to propose a homolytic mechanism.

1) $\overset{+}{\text{ArI}}\text{Ar}' + 2H_2O \longrightarrow \underset{\displaystyle\text{OH}}{\text{ArI}}\text{Ar}' + H_3O^+$

2) $\underset{\displaystyle\text{OH}}{\text{ArI}}\text{Ar}' \longrightarrow \left\{\begin{array}{l}\text{ArI} + \overline{\text{Ar}'\cdot + \cdot\text{OH}} \\ \overline{\text{Ar}\dot{\text{I}}\text{Ar}' + \cdot\text{OH}} \\ \overline{\text{Ar}\cdot + \text{Ar}'\dot{\text{I}}\text{OH}}\end{array}\right. + \left\{\begin{array}{l}\text{Ar}'\text{I} + \overline{\text{Ar}\cdot + \cdot\text{OH}} \\ \overline{\text{Ar}\dot{\text{I}}\text{Ar}' + \cdot\text{OH}} \\ \overline{\text{Ar}'\cdot + \text{Ar}\dot{\text{I}}\text{OH}}\end{array}\right.$

$\text{ArI} + \text{Ar}'\text{OH} \qquad\qquad \text{Ar}'\text{I} + \text{ArOH}$

Step 1 is the formation of a covalent iodonium hydroxide; such covalent hydroxides have never been isolated, although their existence as intermediates in other reactions has been postulated (42). It is well known that tricovalent iodine compounds containing one or more organic ligands are generally unstable (43), so that an iodonium hydroxide might be expected to homolytically decompose in an indiscriminate manner. Rapid recombination of the radicals in the geminate pairs would lead to a near equal distribution of both possible iodides or of both possible phenols.

Although he does not explicitly discuss the case of the nucleophile water, Beringer pictures the hydrolysis to be somewhat different from that just presented (44). He views the reaction of unsymmetrical diaryliodonium salts with nucleophiles as proceeding via two competing mechanistic pathways: (a) a concerted S_N2 attack of the nucleophile at the most electron-deficient carbon, and (b) radical transfer from nucleophile to iodine, followed by substituent-insensitive product-determining steps. The latter mechanism should be favored when the iodonium substituent is overall electron donating (such as 4-CH_3O), and also when the nucleophile is not highly nucleophilic. A large spread in the values of the ratio of nitrophenylation to phenylation was found for a set of nucleophiles, indicating the dominance of the S_N2 mechanism in this system.

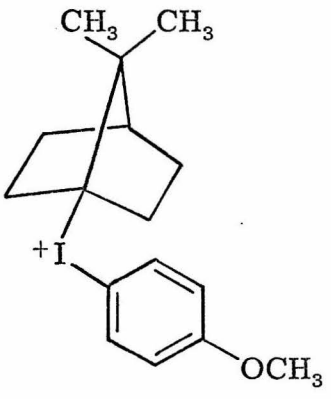
The behavior of weak nucleophiles for the nitro system can be interpreted either as effective competition between two pathways as Beringer suggests, or as substitution by a largely S_N2 pathway in

which the effect of the electronic sensitivity of the substituent ($4-NO_2$) is counterbalanced by the effect of 4-nitroiodobenzene being a better leaving group than iodobenzene. Unfortunately, Beringer and Falk (44) did not do any kinetic studies; only product ratios were determined, and these were estimated by infrared spectroscopy. Further, a sufficiently large enough set of nucleophiles was not really examined. It would be interesting to see how well rates of substitution correlate with the parameters of the Edwards equation (45). This equation may be written as

$$\log (k_n/k_o) = \alpha E_n + \beta H \qquad (I-5)$$

where the nucleophilicity parameters E_n and H relate to the reducing potential and the basicity of the nucleophile, respectively, and α and β are substrate sensitivity parameters.

It was felt that interesting results should be obtained by employing iodonium salts in which one of the ligands is cyclopropyl, 7,7-dimethyl-1-norbornyl or 9-triptycyl, since in these cases there can be little contribution arising from attack by the nucleophile on the aliphatic centers. The reaction of iodonium salt (XVIII) with weak nucleophiles such as water or others should nevertheless yield significant amounts of 1-apocamphanol, according to either the picture of Caserio, Glusker, and Roberts (27), or of Beringer and Falk (44). Strong nucleophiles, according to Beringer's scheme, would not be expected to attack the p-anisyl ring, but since nucleophilic

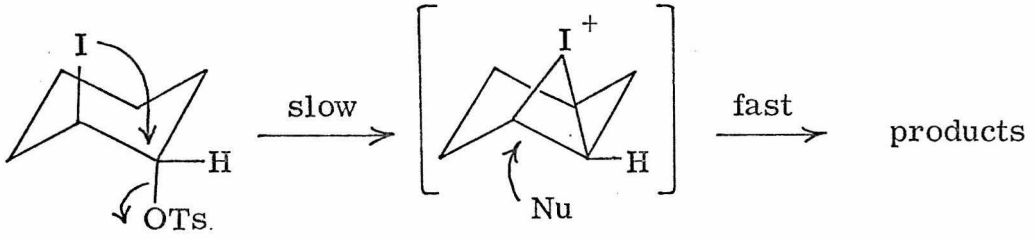


(XVIII)

displacement at the norbornyl carbon is sterically prohibitive, this should show up as a smaller value of β and a larger value of α for this salt than for the 4-methoxydiphenyliodonium salt.

III. Results and Discussion

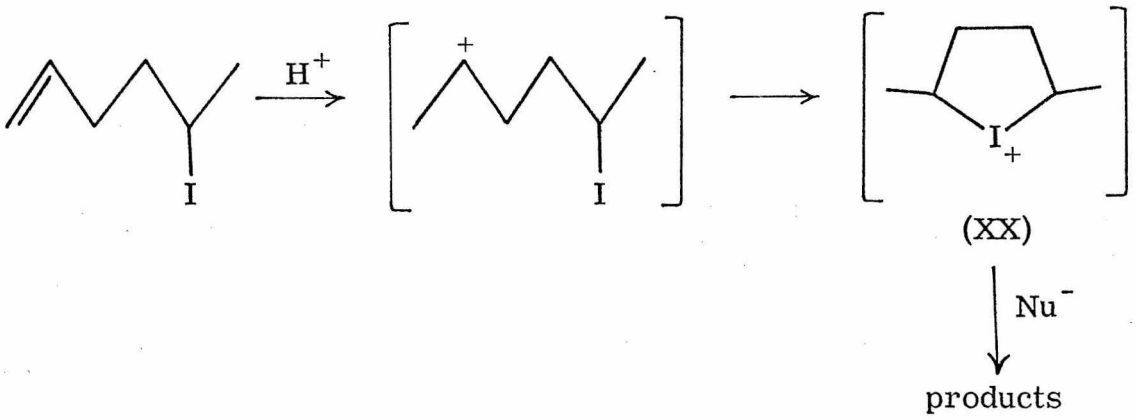
We may ask whether there is any experimental evidence bearing on the existence of aliphatic iodonium ions. The enormous 10^3-fold reactivity of trans-2-iodocyclohexyl tosylate over cis-2-iodocyclohexyl tosylate toward acetolysis strongly suggests participation of the neighboring iodine to give a cyclic three-membered iodonium cation as an intermediate; this is then subject to rapid attack by nucleophiles to give the observed products (46).



(XIX)

Iodonium ions have been postulated as likely intermediates in the additions of certain positive iodine compounds to olefins. Thus, iodine azide (prepared from sodium azide and iodine monochloride in dimethylformamide) adds stereospecifically trans to olefins and in good (60-80%) yield (47). The existence of cyclic five-membered aliphatic iodonium ions has been implicated in the recent work of Peterson and co-workers. Their rate data for the addition of trifluoroacetic acid to 5-halo-1-hexenes (48, 49), or for the solvolysis of

ω-halo-2-alkyl tosylates (50, 51) are interpreted in terms of iodonium intermediates, as illustrated by the example below.



Spectroscopic evidence for the existence of cyclic aliphatic iodonium cations has been obtained by Olah and co-workers (52). If a 2-halo-3-iodo-2, 3-dimethylbutane be dissolved in "magic acid" at -60°, the proton nmr spectrum shows only one methyl singlet; no change in the spectrum occurs upon lowering the temperature to -100°. When the iodine is replaced by fluorine, the nmr spectrum at -60° consists of two singlets, indicating rapid exchange between two nonbridged forms.

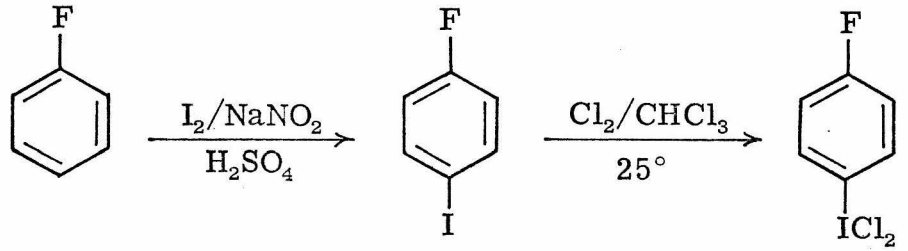
These observations lend additional credence to the belief that aliphatic iodonium salts should be reasonably stable species, provided one eliminates possible nucleophilic pathways that could lead to carbon-iodine bond cleavage. It was decided to commence work by attempting the preparation of salts of the type $[\, C_6H_5IG \,]^+X^-$, where G is an alkyl group. In such salts the phenyliodonio group would be expected to

behave as a strong, inductively electron-withdrawing group (-I), but in order to completely characterize the group, the method popularized by Taft and co-workers was employed (53). According to this method, a group G is electronically characterized by looking at the fluorine-19 nmr resonances for <u>meta</u>- and <u>para</u>-fluoro-substituted C_6H_5G. The resonance and inductive constributions to the <u>sigma</u> constant for the group G are then given empirically by the following chemical shift relationships:

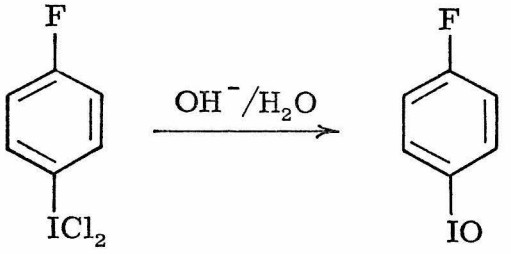
$$\sigma_R^o = \left[\int_H^{\underline{m}\text{-G}} - \int_H^{\underline{p}\text{-G}} \right] \times 0.0339 \qquad \text{(I-6)}$$

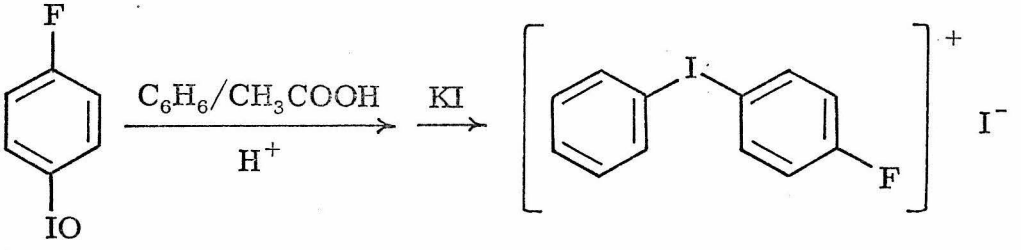
$$\sigma_I^o = 0.0845 - 0.141 \times \int_H^{\underline{m}\text{-G}} \qquad \text{(I-7)}$$

For the purposes of the present investigation, 3-fluorodiphenyliodonium and 4-fluorodiphenyliodonium salts were required. The first salt prepared was 4-fluorodiphenyliodonium iodide, synthesized by the procedure outlined in Figure 4. This salt proved to be insoluble in nearly all common solvents except dimethyl sulfoxide. The insolubility of diphenyliodonium halides in water and other solvents is reminiscent of the solubility properties of the silver halides. For this reason, and also for the reason that the full effect of the phenyliodonio group would be felt if a less nucleophilic anion were present, it was decided to prepare the 3-fluoro- and 4-fluoroiodonium trifluoroacetates. Their syntheses are outlined in Figure 5. These salts were soluble in water, acetonitrile, dimethyl sulfoxide, and numerous other solvents.



(XXI)





(XXII)

Figure 4. Synthesis of 4-fluorodiphenyliodonium iodide

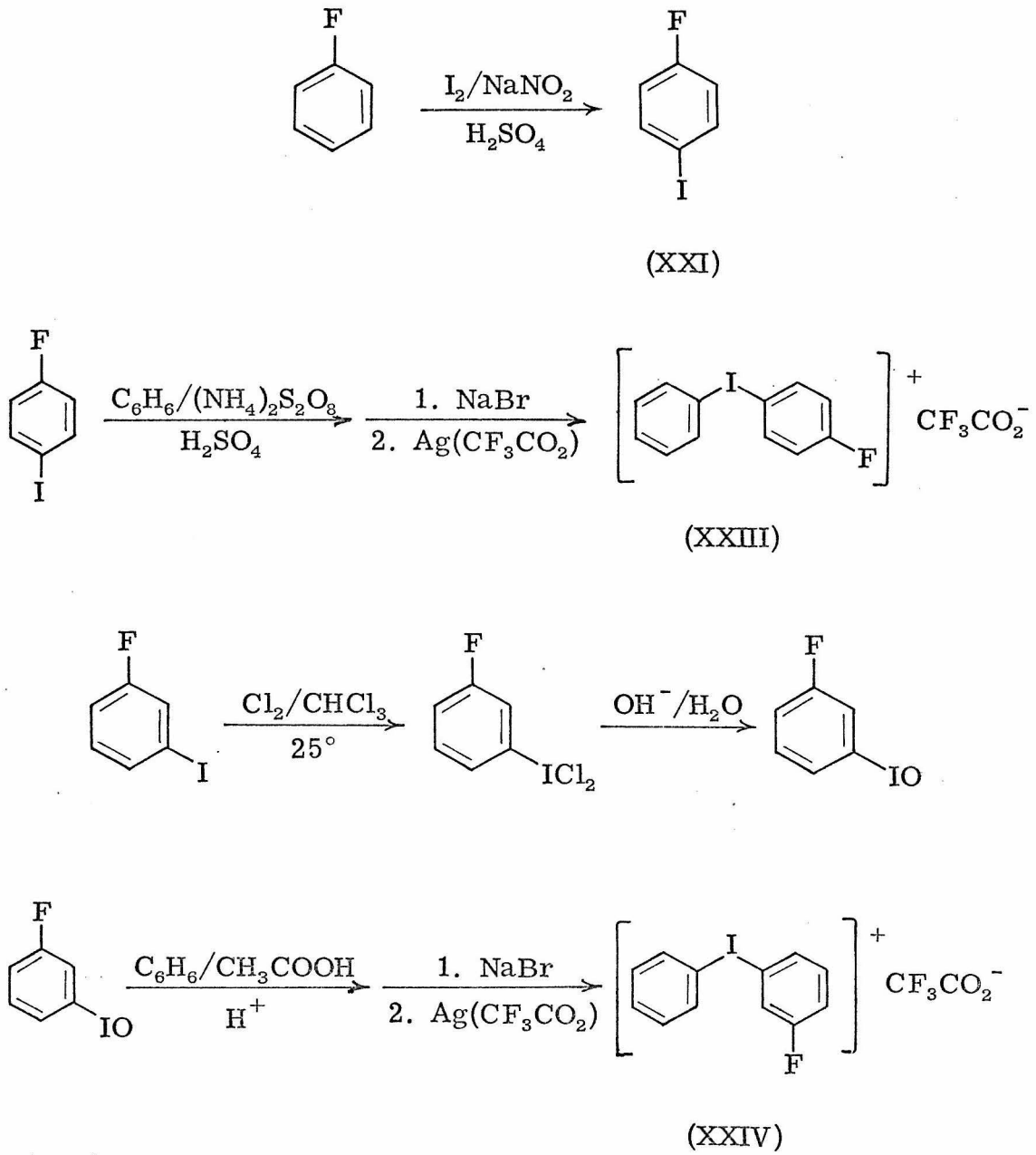


Figure 5. Synthesis of 4-fluoro- and 3-fluorodiphenyliodonium trifluoroacetate

Fluorine-19 nmr spectra were taken in the last two solvents and are recorded in Table 3.

Table 3. ^{19}F-Nmr data for Some Diphenyliodonium Salts[a]

Compound	$\delta_{CFCl_2CFCl_2}$ (int)	Solvent	$\delta_{C_6H_5F}$ (calc)	Solvent
C_6H_5F	46.4	CH_3CN		
(XXI)			-1.5	DMSO
(XXII)			-5.9	DMSO
(XXIII)	39.2	DMSO		
	39.6	CH_3CN	-6.8	CH_3CN
(XXIV)	40.1	DMSO		
	40.6	CH_3CN	-5.8	CH_3CN

[a] Data in ppm; negative numbers mean shifts to lower field.

Using the equations of Taft and the data for the solvent acetonitrile, one can calculate values for σ_R^o and σ_I^o. These results are shown in Table 4, where values of these parameters for a few additional groups are also included (54). The relationship between the σ_R^o and σ_I^o values which one employs for <u>para</u> and <u>meta</u> substituents, are usually formulated as follows (55):

Reactions of $\log (k/k_o) = \rho(\sigma_I^o + \sigma_R^o)$ (I-8)

<u>para</u>-Isomer $= \rho\,\sigma_p$

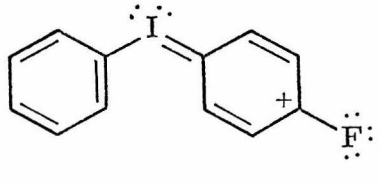
Reactions of $\log (k/k_o) = \rho(\sigma_I^o + \frac{1}{2}\sigma_R^o)$ (I-9)

<u>meta</u>-Isomer $= \rho\,\sigma_m$

Table 4. Hammett σ-Constants for the $C_6H_5I^+$ Group and Other Groups

Group	σ_I^o	σ_R^o	σ_p	σ_m
CH_3O	0.29	-0.42	-0.13	0.08
NO_2	0.60	0.14	0.74	0.67
CH_3	-0.08	-0.12	-0.20	-0.14
$C_6H_5I^+$	0.90	0.03	0.93	0.92

It can be concluded that the phenyliodonio group exerts a strong electron-withdrawing inductive effect, and only a very small electron-withdrawing resonance effect. This means that structures of the form



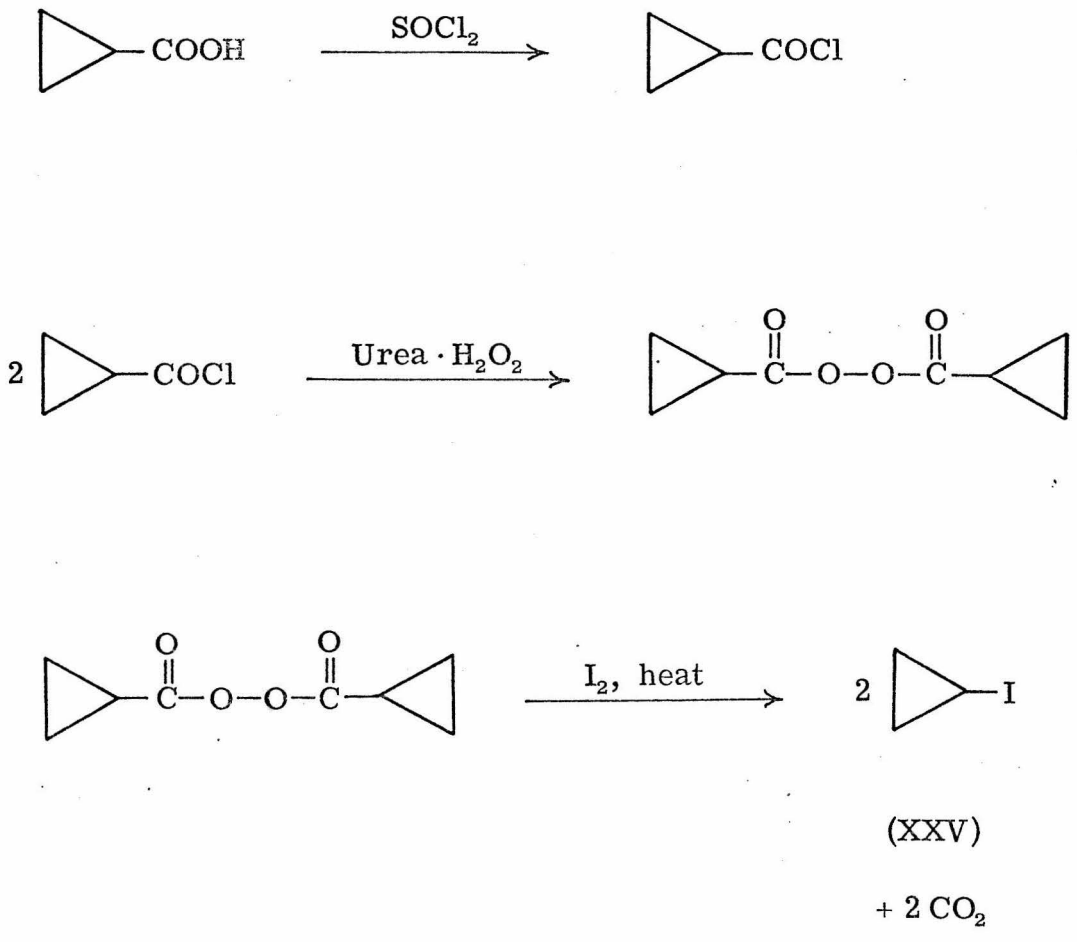
should be of little importance. Maciel has characterized the $-ICl_2$ group in a similar manner; his data yield values of $\sigma_R^o \sim 0.00$ and $\sigma_I^o = 1.10$ (56). The more interesting -IO group has not yet been electronically characterized, presumably because the iodoso derivatives are very insoluble in most solvents.

At the offset, it was felt that an appropriate method for synthesizing partially-aliphatic iodonium salts would be the condensation of an iodoso derivative with an aromatic substrate (see method 4 in Section I). Thus, a suitable combination would be iodosocyclopropane and benzene. Cyclopropyl iodide, 1-iodoapocamphane and 9-iodotriptycene were therefore required, and these were synthesized by the methods outlined in Figures 6-8.

Cyclopropyl iodide was best prepared by converting cyclopropanoyl chloride to the dialkylperoxide, and then decomposing this in the presence of iodine. Attempted Hunsdiecker reactions on cyclopropanecarboxylic acid either gave very low yields or no yields at all of the iodide.

1-Iodoapocamphane was made with some labor starting from the readily available Reychler's acid. Wedekind discovered many years ago that the corresponding camphor-10-sulfonyl chloride undergoes an oxidative carbon-sulfur bond cleavage with alkaline permanganate to give ketopinic acid (57). Wolff-Kishner reduction followed by a Hunsdiecker reaction gave the camphoraceous iodide in good yield.

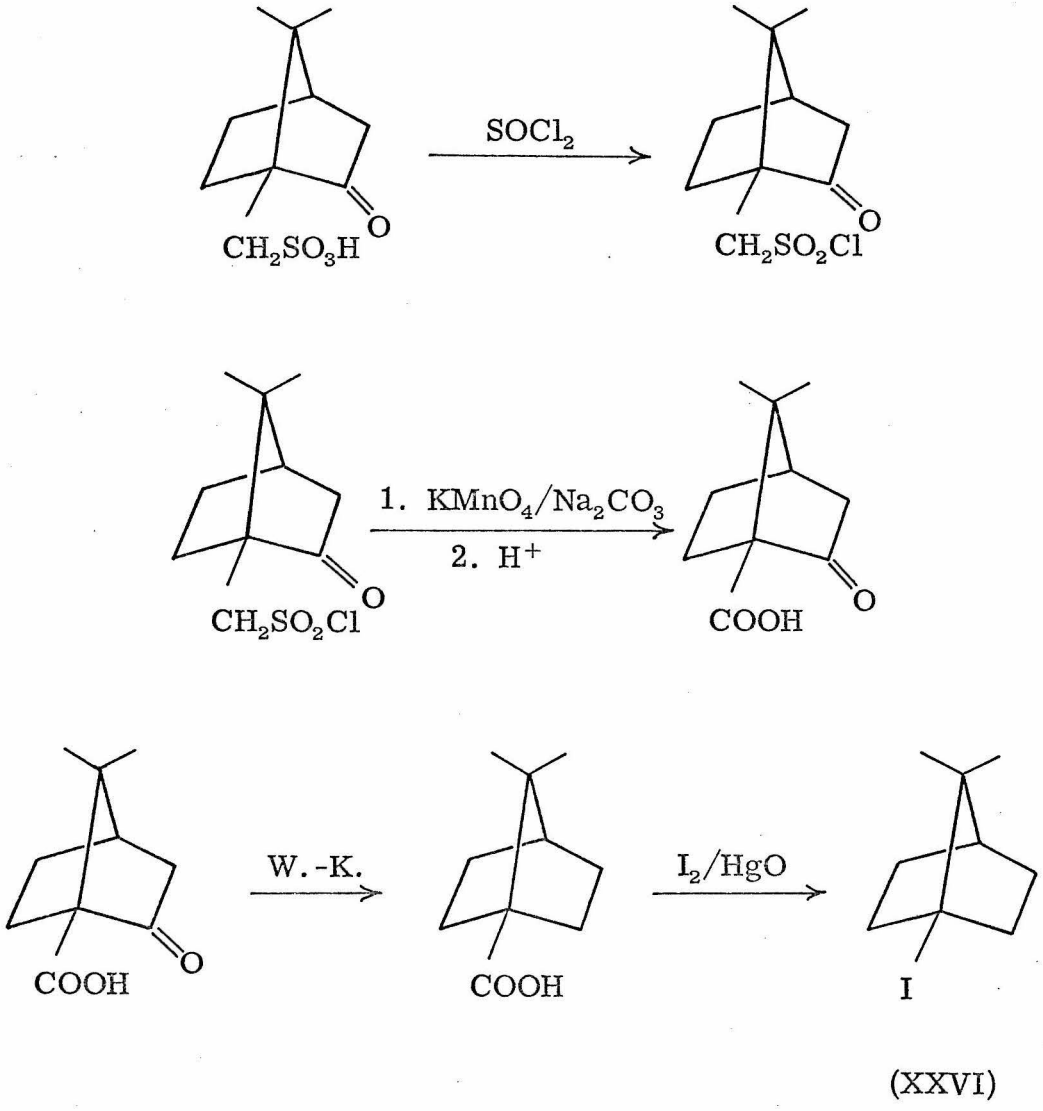
9-Iodotriptycene proved to be more difficult to prepare. This material had actually been prepared many years ago by Bartlett and



(XXV)

+ 2 CO_2

Figure 6. Synthesis of cyclopropyl iodide



(XXVI)

Figure 7. Synthesis of 1-iodoapocamphane

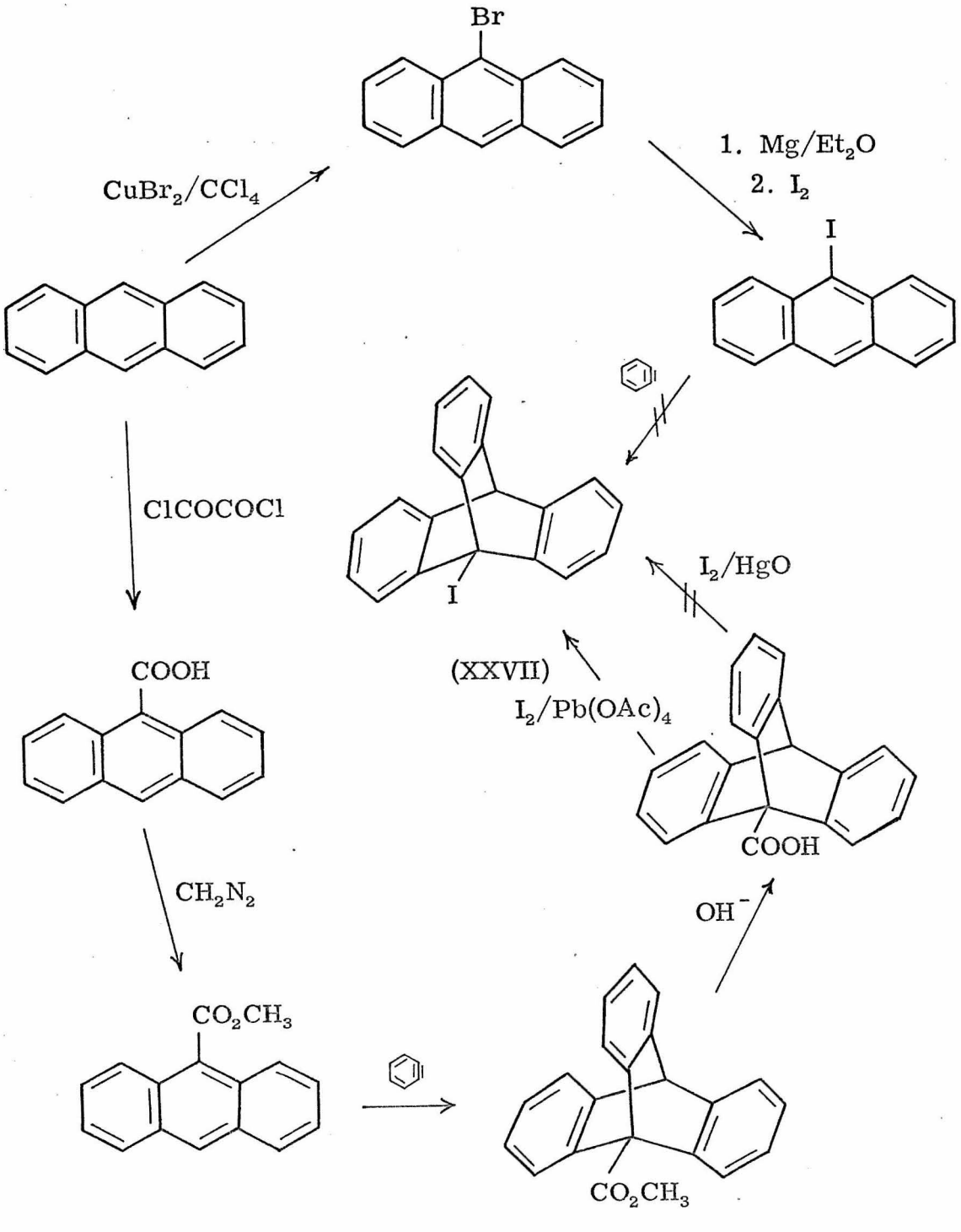
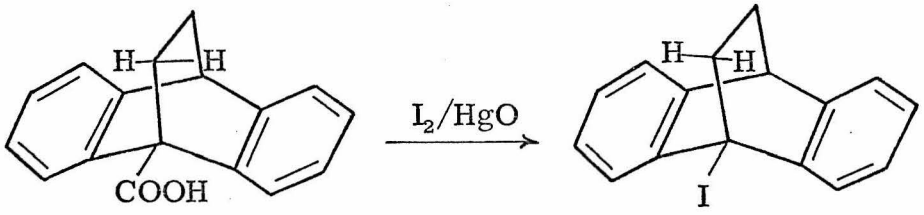


Figure 8. Synthesis of 9-iodotriptycene

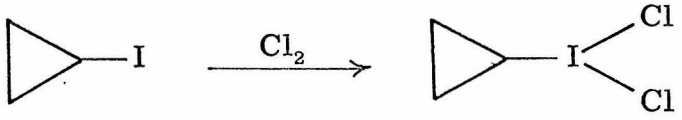
Greene by an elegant 10-step synthesis (58). The overall yield was low, and it was therefore desirable to find a shorter, more practical route. The variety of ways now available for preparing benzynes suggested that an obvious entry into the triptycene system would be via addition of benzyne to an appropriately substituted anthracene. The reaction of benzyne with 9-iodoanthracene did not prove to be a clean reaction, and much better results were obtained in benzyne-additions to 9-carbomethoxyanthracene (59). Saponification of the adduct yielded triptoic acid, but this failed to undergo a Hunsdiecker reaction. Iodinative decarboxylation was finally accomplished using the iodine -- lead tetraacetate reagent which Barton has popularized (see Experimental Section).

The first reaction to which all three iodides were subjected is low-temperature chlorination. No reaction could be induced to occur in the case of 9-iodotriptycene; it may be that this is the result of trying to force two chlorine atoms into the close vicinity of an iodine atom that is sterically shielded by three neighboring aromatic hydrogens. In an attempt to partially remedy this situation, 9,10-dihydro-9,10-ethano-9-iodoanthracene (XXVIII) was prepared from the corresponding acid by a Hunsdiecker reaction. This iodide should have one less serious hydrogen-iodine interaction than 9-iodotriptycene; low-temperature chlorination of (XXVIII), however, failed to yield any of the expected iododichloride.

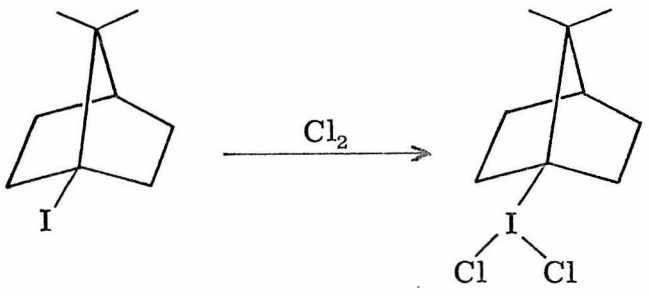


(XXVIII)

Iodides (XXV) and (XXVI), on the other hand, gave upon chlorination in chloroform at -20° goodyields of the orange dichlorides (XXIX) and (XXX).



(XXIX)

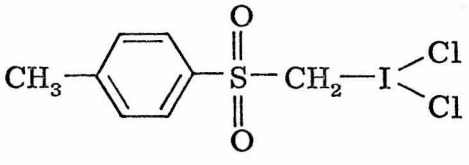


(XXX)

These substances proved to be unstable and had to be transferred rapidly when working at room temperature. They were best stored in a sealed container at temperatures below 0°. When allowed to stand exposed to the air for a short period, the iododichlorides underwent complex decomposition to give dark materials which were never identified. If a chloroform solution of (XXX) were allowed to stand overnight, some 1-iodoapocamphane could be recovered.

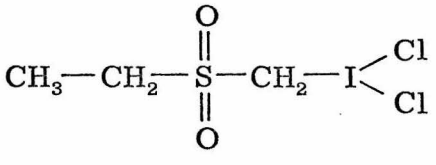
It is interesting to note that Thiele reported iodomethane dichloride, iodoethane dichloride, and the dichloride derived from methylene iodide to be stable below -28°, -36°, and -11°, respectively (60). More recently, Exner has made the dichlorides of some α-iodosulfones; these dichlorides, (XXXI) and (XXXII), are stable solids at room temperature (61), a fact which Exner ascribes to the

(XXXI)



mp 128°

(XXXII)

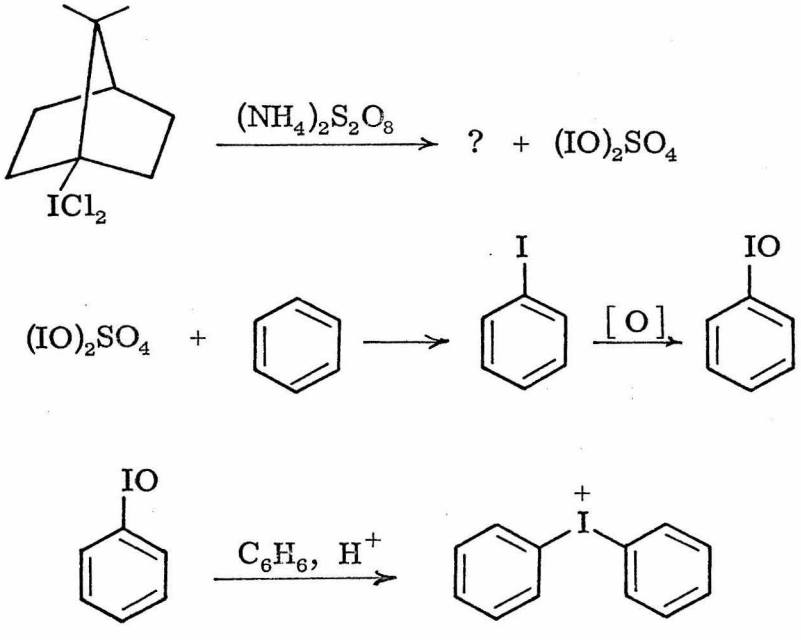


mp 91-93°

neopentyl-type character of the sulfonyl system that would tend to sterically inhibit S_N2 reactions at the methylene carbon. The comparative instability of (XXIX) and (XXX) casts doubt on this explanation. A more likely explanation may be related to the strong inductively electron-withdrawing effect ($\sigma_I^o \sim 0.6$) of the sulfonyl group.

Exner found that (XXXI) and (XXXII) do not yield the corresponding iodoso derivatives when hydrolyzed in aqueous base. Similarly, iododichlorides (XXIX) and (XXX) failed to produce the desired iodoso derivatives. The basic hydrolysis proved to be complex inasmuch as elemental iodine was a product of the reaction (identified with starch indicator), thus indicating cleavage of the carbon-iodine bond. The fate of the carbon skeleton in both cases would have made an interesting subject for study, but was not pursued.

An alternative method for preparing iodoso derivatives is treatment of an iodide with an appropriate oxidizing agent such as ammonium persulfate or peracetic acid. These reagents were ineffective on 9-iodotriptycene; with (XXV) and (XXVI) no solid iodoso derivatives could be isolated, although in the case of (XXV) it was apparent that extensive decomposition had occurred (possibly ring-opening). The oxidation of (XXVI) was attempted in the presence of benzene in the hope that any transient 1-iodosoapocamphane would condense to yield the iodonium salt. The only iodonium salt that could be isolated was a small amount of diphenyliodonium iodide. This necessarily requires cleavage of the carbon-iodine bond; in sulfuric acid the iodine might be converted to iodyl sulfate, which is a good iodinating agent.



One tentative conclusion which may be drawn from these observations is that the aliphatic iodoso derivatives are less stable relative to the starting iodide than are their corresponding iododichlorides. Although several ethylenic iododichlorides are known, Willgerodt reports only one case where the dichloride was converted to a stable iodoso derivative, in this case to ClCH=CH—IO (62).

It is apparent that different synthetic methods are needed in order to successfully prepare the aliphatic iodonium salts. Nesmeyanov and Freidlina reported in 1950 that phenyltrichlorotin is an excellent phenylating agent and will arylate trivalent iodine compounds to give iodonium salts (63). Later, Beringer explored the analogous chemistry with aryllithium derivatives (64). Thus, the reaction of an aryllithium with an aryl iododichloride at low

temperature gives a good yield of the diaryliodonium chloride. In such reactions one usually observes the transient formation of a yellow intermediate which is believed to be a triaryliodine.

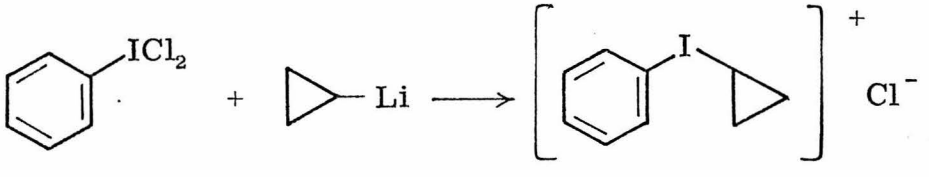
$$ArLi + ArICl_2 \longrightarrow [ArIAr]^+Cl^- + LiCl$$

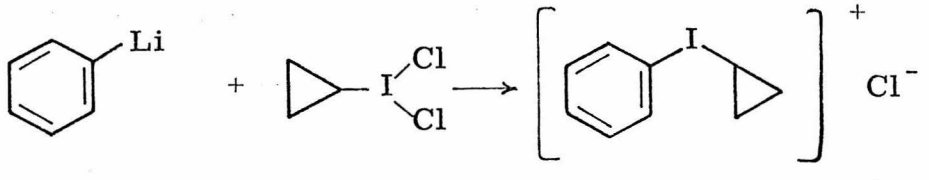
$$ArLi + [ArIAr]^+Cl^- \longrightarrow Ar_3I + LiCl$$

$$Ar_3I + ArICl_2 \longrightarrow 2[ArIAr]^+Cl^-$$

The somewhat milder work-up procedure employed in the lithium case suggested this as the preferred method.

Two sets of experiments were performed with the cyclopropane system. Either cyclopropyllithium was treated with iodobenzene dichloride (A) or phenyllithium was treated with iodocyclopropane dichloride (B). In each case,

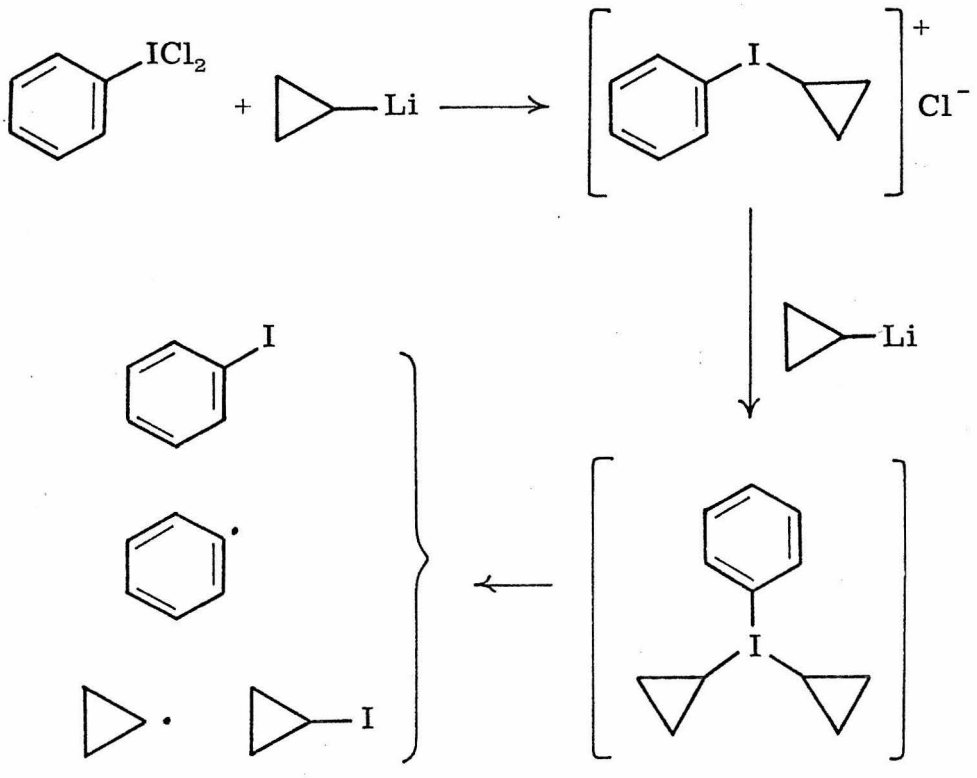
(A) 

(B) 

reaction was carried out at low temperature in ether solution. The organolithium reagents were generated by reaction of lithium wire with

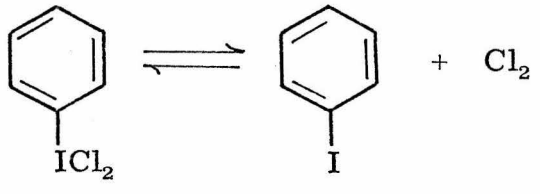
the appropriate bromide in ether. When reaction with the iododichloride was deemed complete, the manner of work-up used was to allow the suspension to warm up to nearly room temperature, dissolve all precipitated salts in water, and then reprecipitate any iodonium salt by the addition of aqueous potassium iodide or bromide.

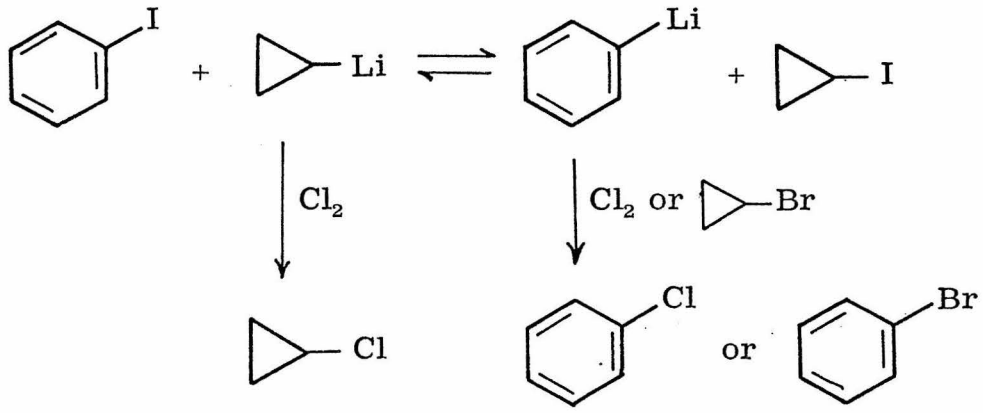
The results can be summarized by stating that in neither set of experiments was any iodonium salt isolated by this method. Examination of the ether solution in the case of reaction (A) revealed the presence of chlorocyclopropane, bromocyclopropane, iodocyclopropane, chlorobenzene, bromobenzene, and iodobenzene. There was no unconsumed iodobenzene dichloride. Since the main purpose of the experiment was synthetic in nature, further studies on it were not carried out. Nevertheless, it is interesting to speculate on the origins of the products. The presence of iodocyclopropane clearly shows that there has been some transfer of iodine. It is tempting to ascribe this to the transient formation of a phenylcyclopropyliodonium salt, which then proceeds to form the triiodine derivative (XXXIII) in accordance with the Beringer mechanism. Such a triiodine would be expected to be very unstable and should undergo homolysis as shown below.
No phenylcyclopropane was present in the ether solution according to the VPC analysis. However, the phenyl and cyclopropyl radicals might well undergo abstraction reactions at a faster rate than for combination.



(XXXIII)

An alternative explanation for the various products is dissociation of iodobenzene dichloride to chlorine and iodobenzene followed by a series of halogen-metal interchanges.





Reaction between iodobenzene dichloride and triptycyllithium also proved to be disappointing. The lithium reagent was prepared by treatment of 9-bromotriptycene with butyllithium in a solvent mixture of benzene and ether (65, 66). Complete reaction took place at -70° as evidenced by the consumption of the iododichloride. When the system was allowed to warm up to about 5°, a white solid precipitated that was filtered and washed with water. This solid proved to be 9-bromotriptycene; addition of aqueous potassium iodide produced only a small amount of diphenyliodonium iodide, probably arising from a series of exchange reactions. The ether--benzene solution contained, as expected, a mixture of halides, in this case, 9-bromotriptycene, 9-iodotriptycene, chlorobenzene and iodobenzene. The presence of any 9-chlorotriptycene would probably have been missed.

IV. Conclusions

The failure to isolate stable aliphatic iodonium salts together with the thermodynamic analysis presented earlier suggests that there are kinetic processes available which either prevent salt-formation under the conditions employed or which rapidly destroy the salts once they are formed. The expected instability of trivalent iodine derivatives containing aliphatic ligands may well be a contributing factor. Although nucleophilic substitution at the aliphatic carbon of the systems employed in this work would presumably not be a serious problem, the aliphatic iodide might well prove to be such a good leaving group that a more-rapid-than-usual substitution at the aromatic carbon could occur. Since chloride ion is present at all times, this would be a difficult process to minimize. However, aryliododifluorides are known compounds, although they are less stable than the dichlorides. Several years ago p-tolyliododifluoride was prepared by treatment of p-tolyliodosobenzene with hydrogen fluoride in acetic acid (67), and more recently, Carpenter has made chloroform solutions of several iododifluorides by reaction of the corresponding iododichloride with hydrogen fluoride and mercuric oxide (68). Since fluoride ion is a fairly weak nucleophile (Swain-Scott nucleophilicity value of 2.0; see ref. 69), it might be possible to achieve greater success by finding suitable conditions to carry out a reaction of the type

$$ArIF_2 + RM \longrightarrow [ArIR]^+F^- + MF.$$

Electrochemical methods were also not examined as a possible means of synthesis. Miller and Hoffmann have shown that anodic oxidation of iodobenzene in a lithium perchlorate -- acetonitrile solution leads to a 45% yield of 4-iododiphenyliodonium perchlorate (70). Alkyl iodides investigated were methyl, isopropyl, t-butyl and neopentyl iodide. These iodides cleaved, however, presumably via the carbonium ions to give N-alkyl acetamides. The alkyl systems used in the present work might be expected to behave differently

$$RI \xrightarrow{-e^-} R^+$$

$$R^+ + CH_3CN \longrightarrow RN{=}\overset{+}{C}{-}CH_3$$

$$RN{=}\overset{+}{C}{-}CH_3 + H_2O \longrightarrow CH_3\overset{O}{\overset{\|}{C}}NHR$$

during the oxidation, particularly since perchlorate ion is a very weak nucleophile.

V. Experimental Section

All melting points and boiling points are uncorrected; the former were taken on a Büchi melting-point apparatus. Infrared spectra were taken on a Perkin Elmer Model IR 237, and the proton nmr spectra were obtained with either a Varian A-60 or A-60A spectrometer. Chemical shifts are reported in ppm downfield from internal tetramethylsilane (δ 0.00). Fluorine nmr spectra were obtained with a Varian A-56/60A spectrometer. Vapor-phase chromatographic analyses were carried out with a Varian Aerograph Autoprep Model 700 instrument. Microanalyses were performed by either Dr. Adalbert Elek, Torrance, California, or by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Cyclopropanoyl Chloride. A 500-ml, three-necked flask was fitted with dropping funnel, magnetic stirrer, reflux condenser and calcium chloride drying tube. In the flask was placed 118 g (1.37 mole) of cyclopropanecarboxylic acid; from the funnel 178.5 g (1.50 mole) of thionyl chloride was added with stirring over a period of 3 hours at room temperature. The solution was stirred overnight, then refluxed for 2-3 hours. Distillation of the black mixture at atmospheric pressure through a Claisen head gave 125.8 g (88%) of colorless liquid, bp 116-118°.

The nmr spectrum consisted of two complex patterns centered at δ 1.2 and 2.1.

Dicyclopropanoyl Peroxide. In a 500-ml Erlenmeyer flask, 230 g (2.03 moles) of 30% hydrogen peroxide was heated to 50-60°. While the temperature was maintained at this point, 80 g (1.33 mole) of urea was added in portions with stirring (71). The solution was kept at 60° for another few minutes, and then the flask was chilled in an ice bath. The white crystals which separated were filtered, dried in air, and stored overnight in an evacuated desiccator. The yield was 65 g (52%). The complex was analyzed for hydrogen peroxide content by titration with permanganate in acid solution (72). It was found to contain 32.7% hydrogen peroxide (calcd 36.2).

In a 1.5-liter, three-necked flask was placed one liter of ether and 61 g (0.59 mole hydrogen peroxide) of urea-peroxide complex. As the solution was stirred with a Hershberg stirrer at 0°, there was added from the funnel 113 g (1.14 mole) of cyclopropanoyl chloride. This addition was carried on fairly rapidly, and was then followed by the addition of 90.5 g (1.15 mole) of pyridine over a period of one hour. After being stirred overnight, the suspension was filtered and the precipitate washed. The combined filtrate and washings were concentrated to 600 ml, then shaken four times with 100-ml portions of water and finally dried over sodium sulfate. Concentration to about 100 ml yielded snow-white crystals, mp 75-77°. The yield was 52.6 g (54%).

Cyclopropyl Iodide. In a 200-ml, three-necked flask, fitted with condenser and dropping funnel, was placed 50.8 g (0.200 mole) of powdered iodine and 20 ml of bromobenzene. The flask was then immersed in an oil bath preheated to 105-110°, and from the funnel

was slowly added a solution of 22.5 g (0.132 mole) of dicyclopropanoyl peroxide in 80 ml bromobenzene. After a short induction period of 15-20 minutes, gas evolution began and continued rapidly for about 3 hours. Occasional manual shaking was found advisable. The mixture was then cooled and the liquid decanted from a residue of iodine. It was diluted with 100 ml of pentane and shaken several times with aqueous sodium bisulfite; even after this treatment the organic layer remained brown. Finally, it was shaken with aqueous sodium carbonate and allowed to stand overnight over a mixture of Norite A and anhydrous sodium sulfate.

Most of the pentane was removed at a rotary evaporator. The remaining solution was then fractionated directly through a 24-inch spinning-band column. Cyclopropyl iodide came over as a nearly colorless liquid, bp 97-98° (lit.(73) 92-93°). The yield was 17.0 g (38%).

The nmr spectrum consisted of two complex patterns centered at δ 1.0 and 2.3.

DL-10-Camphorsulfonyl Chloride. A mixture of 4.64 g (0.020 mole) of DL-10-camphorsulfonic acid (Reychler's acid) and 9.52 g (0.080 mole) of fresh thionyl chloride was heated to reflux in a 50-ml micro flask for 1.5 hours, after which time hydrogen chloride evolution appeared to have practically ceased. After the contents had cooled somewhat, they were quickly poured with vigorous manual stirring onto crushed ice. The major lumps were broken up and then the solid was filtered. The solid was dried in an evacuated desiccator, and the

yield was determined to be 4.53 g (90%) of white crystals, mp 81-83° (lit.(74) 81-83°).

The infrared spectrum showed strong absorptions at 2990, 2930, 1750, 1370, and 1165 cm^{-1}. The nmr spectrum showed sharp singlets at δ 0.93 and 1.15, an unresolved multiplet at δ 1.33-2.66, and a very beautiful AB quartet centered at δ 3.93. Analysis of the quartet yielded chemical shift values of δ 3.67 and 4.20, and a coupling constant of 15 Hz.

The above procedure was repeated with 116 g (0.50 mole) of sulfonic acid and 238 g (2.00 mole) of thionyl chloride. After work-up, there was obtained 158.5 g (essentially quantitative) of slightly moist material which was used immediately without further purification.

DL-Ketopinic Acid. In a three-liter beaker was placed 125 g (1.18 mole) of anhydrous sodium carbonate and 1000 ml of water, and the mixture was heated until it was almost boiling. A mixture of 120 g (0.76 mole) of potassium permanganate and 720 ml of water in a one-liter Erlenmeyer flask was also heated until the solution was near boiling. The carbonate solution was stirred with a blade stirrer and one-third of the potassium permanganate was added, followed by about 53 g of DL-10-camphorsulfonyl chloride. After 10 minutes of heating and stirring, another one-third of the oxidant followed by another 53 g of acid chloride was added; 10 minutes later the remaining portions of oxidant and acid chloride were added. The mixture was heated and stirred for an additional hour; then excess permanganate was destroyed by adding solid sodium bisulfite. After the muddy suspension had

cooled somewhat, it was made strongly acidic with 500 ml of 20% w/w sulfuric acid. The mixture was heated again and the suspended manganese dioxide dissolved by adding teaspoonsful of sodium sulfite. It was necessary to add more sulfuric acid in order to maintain acidity. The slightly pink solution was allowed to cool overnight.

Insoluble solids were filtered off and recrystallized from boiling water to give 15 g (16%) of white material. The pink filtrate from above was extracted five times with 250-ml portions of ether. The ether extracts were combined, shaken with saturated sodium chloride solution, dried over sodium sulfate, and evaporated on a rotary evaporator. The white residue weighed 11 g (12%) and had a melting point of 238-239°. In two later repetitions of this preparation, yields of 30.5 g (33%) and 25.1 g (27%) were obtained.

The infrared spectrum showed strong absorption bands at 3500-3000, 2995, 2945, 1750, 1700, 1415, and 1385 cm^{-1}.

Apocamphane-1-carboxylic Acid. To 45 ml of triethylene glycol in a 100-ml, three-necked flask was added 5.0 g (0.027 mole) of DL-ketopinic acid and 5.6 g (0.100 mole) of potassium hydroxide pellets. Magnetic stirring was begun and the contents were heated at 45° in an oil bath. When the acid had completely dissolved there was then added 5.0 ml (0.103 mole) of 99% hydrazine hydrate. Stirring and heating at 45° were continued overnight under a blanket of nitrogen.

The temperature was then raised to 120-125° and heating and stirring continued for 2.5 hours. The temperature was then lowered to 100° and the solution pumped on at the aspirator until it turned

milky. The bath temperature was then raised to about 210°, at which point gas evolution was brisk. This temperature was maintained for 3 hours. The mixture was then cooled and poured onto 100 g of crushed ice. After filtration of any undissolved solids, the solution was acidified with 1:3 aqueous sulfuric acid. A voluminous white precipitate formed which was allowed to settle overnight.

After filtration and recrystallization from 50% ethanol there was obtained 3.6 g (80%) of white crystals, mp 221-222°. When this preparation was repeated using 81.6 g (0.448 mole) of DL-ketopinic acid, 70 ml (1.46 mole) of 99% hydrazine hydrate and 82.0 g (1.46 mole) of potassium hydroxide pellets in 600 ml of triethylene glycol, there was obtained 80 g (quantitative) of acid, mp 221-222° after recrystallization from 50% aqueous ethanol.

The infrared spectrum showed strong absorption bands at 3400-3000, 2930, 2850, 1685, 1465, 1450, 1300, and 935 cm^{-1}.

1-Iodoapocamphane. A one-liter, three-necked flask was fitted with magnetic stirrer, reflux condenser and Y-tube. In the flask was placed a mixture of 18.3 g (0.080 mole) of red mercuric oxide and 200 ml of cyclohexane. Stirring and refluxing were begun while 25.9 g (0.154 mole) of apocamphane-1-carboxylic acid in 175 ml of cyclohexane was slowly added from a dropping funnel. The apparatus was now covered with toweling and 40.0 g (0.158 mole) of iodine was added in small amounts down the Y-tube over a period of 1.5 hours. More cyclohexane was occasionally added to make stirring easier. Stirring and refluxing were continued for an additional 3.5 hours.

The purple-colored suspension was then filtered, shaken with aqueous sodium bisulfite and finally water. Unreacted acid was removed by shaking twice with 75-ml portions of 2M sodium hydroxide. After the solution had been dried over sodium sulfate, the cyclohexane was evaporated to give 23.2 g of impure material, mp 96-110°. The infrared showed significant carbonyl absorption, in addition to three other foreign bands.

The material was taken up in pentane and applied to a column containing 15 times its weight of alumina. The column was eluted with pentane and 100-ml fractions were taken. About 20 g (52% yield) of camphoraceous material, mp 129-131° (lit. (75) 130-132°) was obtained.

The infrared spectrum consisted of strong absorption bands at 2935, 2850, 1465, 1380, 1255, 965, 905, and 880 cm^{-1}. The nmr spectrum showed a singlet at δ 1.0 and multiplets at δ 1.1-2.2.

Anal. Calcd for $C_9H_{15}I$: C, 43.20; H, 6.05; I, 50.75. Found: C, 42.76; H, 5.99; I, 49.18.

9-Bromoanthracene. In a two-liter, three-necked flask was placed 50 g (0.282 mole) of recrystallized anthracene, 127 g (0.568 mole) of cupric bromide (oven dried at 100°) and 850 ml of dry carbon tetrachloride. The flask was fitted with a mechanical stirrer and reflux condenser; the reaction mixture was stirred and heated under reflux for 69 hours.

The mixture was cooled and the inorganic salts removed by filtration. The filtrate was then applied to an alumina column, containing 600 g of Merck acid-washed alumina, which had been packed two

days earlier. The column was eluted with carbon tetrachloride, and the resulting yellow solutions were evaporated to dryness on a rotary evaporator. There was obtained 70 g (97%) of yellow crystals, mp 95-97°. Further purification did not seem necessary.

9-Iodoanthracene. A 500-ml, three-necked flask, fitted with magnetic stirrer, dropping funnel, reflux condenser, and calcium chloride drying tube and containing 4.0 g (0.165 g-atom) of magnesium turnings, was flamed out under nitrogen. The magnesium was covered with ether and activated with a small portion of 1,2-dibromoethane. A solution of 22.3 g (0.087 mole) of 9-bromoanthracene in 250 ml of ether was slowly added. When the addition was complete, the solution was refluxed under nitrogen for 24 hours.

Heating was now discontinued and a solution of 26 g (0.102 mole) of iodine in 200 ml of ether was added with stirring. The iodine color quickly disappeared. The yellow, supernatant liquid was decanted and washed successively with water and aqueous sodium bisulfite. Evaporation of the ether left a yellow residue, which was recrystallized from hot 95% ethanol to give 8.0 g (30%) of 9-iodoanthracene, mp 75-77°.

Addition of Benzyne to 9-Iodoanthracene. A 25-ml, three-necked flask was fitted with magnetic stirrer, dropping funnel, reflux condenser and drying tube. A mixture of 1.00 g (3.9 mmole) of 9-iodoanthracene and 0.48 g (4.1 mmole) of isoamyl nitrite in 10 ml of methylene chloride was brought to reflux. Then over a period of 45 minutes a solution of 0.50 g (3.6 mmole) of anthranilic acid in 4 ml of

acetone was added (76). The solution in the flask soon became a deep, dark red. When the addition was complete, stirring and refluxing were continued for another hour. The volatile compounds were removed by distillation and gradually replaced with p-xylene. To the xylene solution was now added 0.2 g (2.0 mmole) of maleic anhydride and the solution refluxed for 15 minutes. The mixture was cooled and then added to 20 ml of cold water, diluted with methylene chloride, and the lower organic layer shaken several times with 3N sodium hydroxide. Treatment with Norite, drying, and then evaporation of the solvent left an amber, unctuous oil which would not crystallize. This was taken up in a 1:5 mixture of chloroform and carbon tetrachloride and chromatographed on 40 g of neutral alumina. The main fraction consisted of 0.53 g of a yellow, crystalline solid, which melted over a large range beginning at 63°. The infrared spectrum was much more complex than would be anticipated for a rigid triptycene system, and in fact, all bands of 9-iodoanthracene were found in the spectrum. The nmr spectrum consisted of a complex pattern of four poorly resolved and imperfectly separated aromatic signals in the region of δ 6.8 to 8.5, and a weak singlet at δ 5.3; the ratio of the integrated areas was approximately 26:1. If the singlet at δ 5.3 be assigned to the lone triptycene bridge-head proton, and if the mixture be presumed to consist only of 9-iodoanthracene and 9-iodotriptycene, then the ratio of these two components is approximately 60:40. No further means of separation was tried.

9-Anthroic Acid. In a one-liter flask was placed successively 70 g (0.39 mole) of powdered anthracene, 210 ml of reagent nitrobenzene and 45 ml (1.05 mole) of oxalyl chloride. The mixture immediately turned orange. A reflux condenser with drying tube was attached and the flask was placed in a metal bath. The temperature of the bath was brought up to 205° in 3 hours and maintained there for 9 more hours. At the end of this time the nitrobenzene was steam distilled from the black mixture and 70 g (1.75 mole) of sodium hydroxide pellets were added. The solution was heated for one hour on the steam bath, and when it had cooled, unconsumed anthracene and a considerable amount of tar were filtered from the mixture. Acidification with 200 ml of concentrated hydrochloric acid produced a voluminous yellow precipitate. Recrystallization of this from 95% ethanol gave 19.0 g (21.8% of acid), mp 225-227° (crop 1), followed by 1.9 g (2.2%), mp 220-222° (lit.(77) 217°). The compound was soluble in dilute sodium carbonate solution.

An infrared spectrum taken in a KBr pellet showed absorption bands at 1675, 1410, 1250, and 910 cm^{-1}.

Methyl 9-Anthroate. In a 250-ml Erlenmeyer flask was placed a solution of 9.8 g (0.175 mole) of potassium hydroxide pellets in 40 ml of water. A layer of 100 ml of ether was poured on top and the whole was cooled in an ice bath. Over a period of 20 minutes there was added with swirling 17.2 g (0.167 mole) of N-methyl-N-nitrosourea. In another flask was prepared a slurry of 9.5 g (0.043 mole) of 9-anthroic acid in 100 ml of ether. The diazomethane solution was now

added portionwise with swirling in the ice bath to the acid. Vigorous gas evolution was evidence of ester formation. Eventually, the slurry became a clear orange solution. The flask was now allowed to come to room temperature and the ether solution was then shaken successively in a separatory funnel with sodium bicarbonate solution, water, and saturated sodium chloride solution. The resulting ether extract was allowed to evaporate in air and afforded 10.6 g (100%) of a dirty, yellow residue. Recrystallization from methanol gave 9.4 g (93%) of yellow crystals, mp 110-111°.

The infrared spectrum showed absorption bands at 3040, 2980, 2930, 1725, 1625, 1440, 1430, 1345, 1285, 1225, 1015, 895, and 860 cm^{-1}.

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.3; H, 5.09. Found: C, 80.94; H, 5.09.

9-Carbomethoxytriptycene. A mixture of 12.0 g (0.051 mole) of methyl 9-anthroate, 7.2 g (0.063 mole) of isoamyl nitrite and 125 ml of methylene chloride was brought to reflux under nitrogen. Over a period of 2.5 hours there was added a solution of 7.5 g (0.054 mole) of anthranilic acid in 50 ml of reagent acetone. Gas evolution was immediate, and after 10 minutes the refluxing solution was quite dark. Refluxing and stirring were continued for another hour. After the solution had sat overnight, the volatile liquids were removed by distillation and replaced with toluene. Unaltered methyl 9-anthroate was destroyed by adding 3.75 g of N-ethylmaleimide and refluxing for one hour. The toluene was then stripped off at a rotary evaporator, leaving a dark

viscous oil.

This dark oil was slurried with a small amount of carbon tetrachloride and applied to a column of 340 g of Woelm neutral alumina which had been packed the day before. The column was then eluted with a 99:1 mixture of carbon tetrachloride -- methanol. Crude material which was obtained in two 200-ml fractions was combined and recrystallized from absolute methanol to give 2.6 g (16%) of white solid, mp 175-180°. An additional recrystallization from absolute methanol gave material, mp 185-190°.

The infrared spectrum showed strong absorption bands at 3025, 2965, 2920, 1735, 1585, 1455, 1250, 1155, and 1020 cm^{-1}.

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.6; H, 5.16. Found: C, 83.88; H, 5.19.

Mol. Wt. Calcd: 312. Found: 316.

Triptoic Acid. A solution of 1.23 g (0.0220 mole) of potassium hydroxide pellets in 20 ml of diethylene glycol was heated to 130°. Then 0.54 g (0.0017 mole) of the 9-carbomethoxytriptycene was added and the solution stirred and heated for 2 hours. The amber solution was then poured into 60 ml of water, treated with Norite, filtered, and acidified with dilute sulfuric acid. The white crystals which formed were filtered and stored overnight in a desiccator. Yield: 0.32 g (62%), mp 352-353°. When the saponification was repeated on a 2.5-g scale of ester, an 83% yield of acid was obtained.

Anal. Calcd for $C_{21}H_{14}O_2$: C 84.5; H 4.73. Found: C 82.40; H 4.86.

Hunsdiecker Reaction on Triptoic Acid. The modified Hunsdiecker reaction of Cristol and Firth was attempted on triptoic acid (78). A 100-ml, three-necked flask was fitted with magnetic stirrer and condenser. A mixture of 2.0 g (6.6 mmole) of triptoic acid, 0.86 g (4.0 mmole) of red mercuric oxide and 50 ml of cyclohexane was stirred and refluxed for one hour. Then over a period of one hour 1.78 g (7.0 mmole) of iodine was added in portions. Refluxing was continued for 70 hours.

The cooled mixture was filtered and the residue washed with cyclohexane. It was then shaken successively with aqueous sodium bisulfite, sodium hydroxide (twice) and saturated sodium chloride solutions. After the solution had been dried over sodium sulfate, the solvent was removed at a rotary evaporator. There remained 0.5 g of a white residue whose infrared spectrum showed the absence of –OH; there was a peak of medium intensity at 1735 cm^{-1} as well as strong peaks at 1460 and 920 cm^{-1}. The nmr spectrum showed a complex pattern of signals at δ 6.8-8.0 and a small unresolved signal at δ 5.3. Scanning showed the absence of any acidic protons. Attempts to sublime a sample of the material in vacuo led to complete decomposition above 150°.

9-Iodotriptycene. A one-liter, three-necked flask was fitted with reflux condenser, dropping funnel and magnetic stirrer. In the flask was placed 6.7 g (0.0225 mole) of triptoic acid, 30.0 g (0.0677 mole) of lead tetraacetate and 300 ml reagent benzene containing 3 drops of acetic anhydride. The suspension was stirred and refluxed under a

blanket of nitrogen, and shortly assumed an orange coloration. From the funnel was then added in 10-ml portions a 0.408 M solution of iodine in benzene. As each portion was added, the flask was irradiated with a 100-watt tungsten lamp, and new portions were not added until after the previous portion had been consumed as evidenced by a change in the color of the suspension from purple to light-orange. Approximately 145 ml (0.059 moles I_2) of solution was consumed.

The solution was now refluxed for another 1.5 hours, after which time the cooled pink suspension was filtered and washed successively with sodium bisulfite, sodium hydroxide, water, and saturated sodium chloride. After the benzene extract had been dried over anhydrous sodium sulfate, the solvent was removed at a rotary evaporator, leaving behind 2.29 g (27%) of a cream-colored solid, mp 249-264°. This was purified by vacuum sublimation at 200° to give 1.97 g (23%) of material, mp 259-265° (lit.(79) 262-265°).

The infrared spectrum showed sharp peaks at 3040, 2975, 2930, 1600, 1450 (doublet), 1280, 1150, and 930 cm^{-1}. The last peak is rather strong; Bartlett observes that triptycene derivatives characteristically have a strong band in this region. In addition, there were three weak but sharp bands in the 1750-2000 cm^{-1} region which displayed a pattern indicative of an ortho-disubstituted benzene (80).

The nmr spectrum ($CDCl_3$) displayed a complex aromatic pattern of signals at δ 6.8-7.9; these were only partially separated into three groups of relative areas 1:1:2. The bridgehead proton appeared as a singlet at δ 5.4.

Experiments with 9-Iodotriptycene. (a) To a stirred suspension of 100 mg (0.263 mmole) of 9-iodotriptycene in 2 ml of concentrated sulfuric acid at 15-25° was slowly added 66 mg (0.290 mmole) of ammonium persulfate, whereupon the suspension shortly turned black. This was followed a few minutes later by 0.5 ml of benzene; stirring at room temperature was continued for 7 more hours. The dark suspension was then poured onto ice, filtered, and the filtrate clarified with Norite. Addition of aqueous sodium bromide produced no precipitate, indicating the absence of iodonium ions. The residue from above was shaken with chloroform, filtered, and evaporated. The infrared spectrum of the residue was identical to that of starting iodide.

(b) A mixture of 100 mg (0.263 mmole) of 9-iodotriptycene, 2 ml of acetic anhydride and 2 ml of peracetic acid was stirred overnight at room temperature. Then to the white suspension was added 0.5 ml of concentrated sulfuric acid and 0.5 ml of benzene. It was cooled in ice water and stirring continued for 3 hours. Work-up was done as in the previous method; again, addition of sodium bromide to the aqueous filtrate produced no precipitate. The filtered residue was dried in air and afforded 0.076 g of white material whose infrared spectrum was identical in all respects to that of 9-iodotriptycene.

(c) A solution of 1.2 g (3.20 mmole) of 9-iodotriptycene in 25 ml of chloroform in a 100-ml, three-necked flask was cooled to -25° and chlorine was passed in for 30 minutes. At the end of this time no precipitate had appeared, so 10 ml of ether was added and passage continued at low temperatures for another hour. After this time no

precipitate was visible; the yellow-green color of the solution gave no indication that the dichloride could possibly have remained in solution.

After the solution had risen to room temperature overnight, the solvent was removed by a rotary evaporator, leaving behind an oil. This was chilled in the freezer for a few hours and eventually a solid crystallized from the oil. The supernatant oil remaining was removed and examined; its nmr spectrum was identical to that of 1,2-dichloroethyl ether plus minor amounts of other possible chlorination products of ether. The precipitated solid was filtered and washed with cold carbon tetrachloride to give 700 mg of solid. Its nmr and infrared spectra were identical to that of starting material.

9,10-Dihydro-9,10-ethano-9-iodoanthracene. (a) Professor J. S. Meek kindly supplied a sample of 9,10-dihydro-9,10-ethanoanthracene-9-carboxylic acid. This material had mp 248-251°; its infrared spectrum showed peaks at 3500-3100 (broad), 3045, 2975, 2925, 1710, 1460 (doublet), and 1275 cm^{-1}.

The Barton method of decarboxylation, which was used in the synthesis of 9-iodotriptycene, was attempted on a small sample of the above acid. A mixture of 0.44 g (1.76 mmole) of acid, 2.3 g (5.2 mmole) of lead tetraacetate and 10 ml of 0.408 M iodine in benzene was refluxed for 3 hours. Work-up was done in the usual manner and afforded 0.29 g (50%) of a light-yellow residue, mp 132-136°. Its infrared spectrum was consistent with structure; in addition, however, an appreciable amount of carbonyl-containing material was also present so that the spectrum was actually a good deal more complex

than that of 9-iodotriptycene.

(b) A 500-ml, three-necked flask was fitted with magnetic stirrer and reflux condenser with drying tube. A stirred mixture of 300 ml of cyclohexane, 6.0 g (0.024 mole) of 9,10-dihydro-9,10-ethanoanthracene-9-carboxylic acid, and 10.8 g (0.050 mole) of red mercuric oxide was brought to reflux. Over a period of one hour 12.4 g (0.049 mole) of iodine was added in portions; the suspension was stirred and refluxed for an additional 25 hours. At the end of this time the suspension was filtered while warm. The cooled filtrate was diluted with 125 ml of ether and shaken successively with sodium bisulfite, potassium iodide, sodium hydroxide (twice) and saturated sodium chloride. Clarification with Norite was followed by drying over anhydrous sodium sulfate.

The filtered solution was evaporated in a rotary evaporator, leaving behind a light-green oil. This could be induced to crystallize at low temperatures. The solid was then taken up in cyclohexane again and applied to a column of 50 g of Woelm neutral alumina. Elution was done with cyclohexane; all of the product emerged from the column in the second and third fractions (50 ml each). It had mp 136-138° and was judged to be pure by the complete absence of any carbonyl-containing material. The total yield was 5.0 g (63%).

The infrared spectrum nevertheless contained more bands in the 800-1600 cm^{-1} range than that of 9-iodotriptycene. Peaks were present at 3045, 2975, 2925, 2845, 1610, 1450, 1290, 1140 (doublet), 1035, 875, and 820 cm^{-1}. In addition, there was a strong band at

915 cm^{-1} which is highly reminiscent of the band used by Bartlett to identify derivatives of triptycene. A very clear set of three bands occurred in the 1750-2000 cm^{-1} range, again consistent with an ortho-disubstituted benzene. The nmr spectrum showed two aromatic patterns of signals centered at about δ 7.1 and 7.7; the four methylene protons appeared as a broad multiplet at δ 1.4-2.5. The lone bridge-head proton was present at δ4.2 as a partly-resolved triplet with J_{HH} = 2.6 Hz. The integration was consistent with structure.

Anal. Calcd for $C_{16}H_{13}I$: C, 57.83; H, 3.95; I, 38.22. Found: C, 57.66; H, 3.97; I, 38.19.

9-Bromotriptycene. The procedure of Friedman and Logullo was again followed. In a 200-ml, three-necked flask was placed 6.2 g (0.024 mole) of 9-bromoanthracene, 3.5 g (0.030 mole) of isoamyl nitrite and 80 ml of methylene chloride. The solution was stirred and refluxed and from a funnel was added a solution of 3.7 g (0.026 mole) of anthranilic acid in 20 ml of dry acetone over a period of 2 hours. After the solution was stirred and refluxed for another 2.5 hours, the solvents were stripped off at a rotary evaporator and replaced by a p-xylene solution of 2.5 g of maleic anhydride. The xylene solution was refluxed for 2 hours more and was then stirred at room temperature overnight.

The dark mixture was diluted with methylene chloride, shaken four times with aqueous sodium hydroxide, then with brine, and finally dried over sodium sulfate. Removal of the solvent left a yellow-brown residue which was then taken up in benzene and chromatographed on

100 g of alumina. From the second 75-ml benzene fraction was obtained 3.5 g (44%) of a yellow solid.

The infrared spectrum of the material showed it to be mainly 9-bromotriptycene, as judged by comparison with a spectrum of material made by Bartlett (81), with perhaps some contamination by 9-bromoanthracene and by triptycene.

The procedure was then scaled up using 25.0 g (0.097 mole) of 9-bromoanthracene, 14.0 g (0.120 mole) of isoamyl nitrite and 15.0 g (0.105 mole) of anthranilic acid. From the second and third 250-ml chromatographic fractions there was obtained 9.5 g (30%) of a yellow, crystalline residue. This was combined with the material made in the small scale run and recrystallized from methylcyclohexane to give 10.9 g of crystals which were tinged yellow; the mp was 250-254°.

The infrared spectrum showed strong bands at 3045, 2980, 2945, 1605, 1455, 1445, 1285, 1155, 1035, and 935 cm^{-1}.

Anal. Calcd for $C_{20}H_{13}Br$: C, 72.07; H, 3.94; Br, 23.99. Found: C, 72.30; H, 4.00; Br, 23.88.

Iodocyclopropane Dichloride. The following experiment is typical for either cyclopropyl iodide or 1-iodoapocamphane. A 100-ml, three-necked flask, fitted with inlet tube and a calcium chloride drying tube, was charged with a solution of 2.43 g (0.014 mole) of cyclopropyl iodide in 20 ml of spectroquality reagent chloroform. Magnetic stirring was begun and the solution was cooled to -50°. Chlorine gas from a cylinder was passed through a tower of concentrated sulfuric acid and then through a large plug of glass wool. From there it was led into the

flask; the tip of the entry tube was kept at about 1-2 cm above the surface of the liquid. Passage was done in dim light. After one hour at -50° there was no evident formation of the expected orange dichloride; this is probably a temperature effect on the rate. The contents of the flask were allowed to warm to -10° and passage continued. After 0.5 hour the dichloride was clearly visible, and after 0.5 hour more the passage was stopped. The orange, precipitated solid was quickly filtered from the chloroform and weighed. The yield was 3.6 g (essentially quantitative). In other runs, the yield usually varied between 80% and 90%. At room temperature, there occurred spontaneous evolution of chlorine from the solid, so that it was necessary to store it in the freezer. After one week in the freezer, extensive decomposition occurred.

Attempted Preparation of Iodosocyclopropane. An approximately 1-g sample of dichloride was placed in a mortar chilled in an ice-salt-water bath. It was covered with 1 g of sodium carbonate and ground together along with 5 drops of water. The mixture began to blacken and when 1 ml of 3N NaOH was added, and grinding continued, the paste was completely black. After the addition of 5 ml more of base and further grinding, the color of the suspension changed to white. Water (20 ml) was added and grinding continued until all solid matter had gone into solution. Tests for iodide and chloride ions were positive; when the solution was extracted with ether and the ether evaporated, no residue of iodoso compound was obtained. The fate of the carbon skeleton was not pursued further. Similar hydrolysis of

1-iodoapocamphane dichloride failed to produce the expected iodoso derivative.

Oxidation of 1-Iodoapocamphane. To a suspension of 4.0 g (0.016 mole) of 1-iodoapocamphane in 80 ml of concentrated sulfuric acid there was added with stirring at room temperature 4.1 g (0.018 mole) of ammonium persulfate. Even before the addition was completed the mixture had passed through successive colors of light-yellow, tan, milky-white, brown, and finally black. At this point, 25 ml of benzene was added and stirred was continued at 5° for 1.5 hour. The mixture was then poured onto cracked ice and filtered. The odor of unchanged 1-iodoapocamphane in the green-black residue was apparent. After the filtrate had been treated with Norite A, a strong solution of potassium iodide was added. A yellow-white precipitate formed which was filtered and dried in a desiccator for 3 days. Its weight was 0.49 g and it had a melting point of 180-185° (dec). Elemental analysis and the nmr spectrum of a dimethyl sulfoxide solution of the compound affirmed that it was diphenyliodonium iodide.

The nmr spectrum (DMSO) showed a multiplet at δ 5.7-6.5.

Anal. Calcd for $C_{12}H_{10}I_2$: C, 35.3; H, 2.48; I, 62.3. Found: C, 35.12; H, 2.57; I, 62.52.

Diphenyliodonium iodide is reported to have a melting point of 181-183° after three recrystallizations from methanol (82).

Experiments with 9,10-Dihydro-9,10-ethano-9-iodoanthracene. (a) A 100-ml, three-necked flask was rigged for chlorination as usual.

A solution of 2.0 g (6.0 mmole) of 9,10-dihydro-9,10-ethano-9-iodoanthracene in a mixture of chloroform and cyclohexane was cooled to -25° and chlorine passed in for one hour. No precipitate appeared even though the mixture had a cloudy appearance.

(b) One attempt was made to oxidatively condense the iodide with benzene. A mixture of 200 mg (0.60 mmole) of iodide, 140 mg (0.62 mmole) of ammonium persulfate, 2 ml of concentrated sulfuric acid and 0.5 ml of benzene was stirred at 5° for 10 hours. Workup was done as previously described; addition of sodium bromide to the aqueous extract gave no precipitate, indicating the absence of iodonium ions.

p-Fluoroiodobenzene Dichloride. p-Fluoroiodobenzene was prepared according to the procedure of Varma et al., by iodinating fluorobenzene with iodine and fuming sulfuric acid in carbon tetrachloride (83). For the chlorination the same apparatus which has been described previously was used. Chlorine gas was passed into a 100-ml flask containing a chloroform solution of 5.0 g (0.022 mole) of p-fluoroiodobenzene. After passage of chlorine for 30 minutes, the product was filtered, washed with chloroform and dried in air. The weight of this crop was 3.9 g. Concentration of the filtrate yielded another 0.5 g of bright-yellow crystals for a total yield of 4.4 g (67%).

p-Fluoroiodosobenzene. The procedure used by Lucas, Kennedy, and Formo for iodosobenzene was followed (84). In a large mortar which was chilled in a large pan of ice there was placed 4.5 g (0.015 mole) of

p-fluoroiodosobenzene dichloride, 4.2 g (0.040 mole) of anhydrous sodium carbonate and 9 g of chopped ice. The mixture was thoroughly ground until a paste resulted and the ice had melted. Then, 9 ml of 6 N sodium hydroxide was added in four portions with trituration after each addition. Finally, 10 ml of water was added and the contents were allowed to sit overnight.

The white precipitate was filtered and washed several times with water. To the filtrate of about 200-ml volume there was added 15 ml of potassium iodide solution, whereupon a light-orange precipitate formed. This was filtered and dried in air; its weight was 0.1 g, mp 195-200° (dec). To confirm that this by-product was 4,4′-difluorodiphenyliodonium iodide, a sample was submitted for analysis. The dried, white precipitate of p-fluoroiodosobenzene weighed 2.6 g (71%).

Anal. Calcd for $C_{12}H_8F_2I_2$: C, 32.5; H, 1.8; I, 57.3. Found: C, 26.79; H, 1.75; I, 62.25.

4-Fluorodiphenyliodonium Iodide. To a cold, stirred solution of 2.6 g (0.011 mole) of p-fluoroiodosobenzene, 6 ml of benzene, 30 ml of acetic acid and 6 ml of acetic anhydride there was added dropwise from a funnel 2.5 ml of concentrated sulfuric acid. A clear solution immediately formed, but shortly thereafter it assumed a yellow color.

After 24 hours of stirring, the mixture was diluted with 50 ml of water, extracted with ether, and to the aqueous layer there was added a strong solution of potassium iodide in water. A brick-orange precipitate formed immediately, which was filtered and washed successively with water and acetone. About 2.2 g of light-tan powder

remained. It was recrystallized from 60-70 ml methanol, to give snow-white crystals, soluble in chloroform. The yield of product was 1.9 g (40%), mp 195° (85).

Anal. Calcd for $C_{12}H_9FI_2$: C, 33.8; H, 2.12; I, 59.7. Found: C, 33.65; H, 2.25; I, 57.90.

Nuclear magnetic resonance spectra of fluorobenzene, p-fluoroiodobenzene and 4-fluorodiphenyliodonium iodide were taken using dimethyl sulfoxide as a solvent and trifluoroacetic acid as the internal standard. The use of dimethyl sulfoxide as a solvent was dictated by the fact that no other common solvent could be found which would dissolve the iodonium iodide. In fact, aromatic iodonium iodides generally behave similarly in many respects to silver iodide; indeed, silver iodide is readily soluble in dimethyl sulfoxide.

m-Fluoroiodosobenzene. Chlorination of m-fluoroiodobenzene, which was obtained from Peninsular Chemical Co., was carried out as described earlier. The light-yellow (almost white) dichloride that was obtained was used immediately for the next step.

Hydrolysis of 14.7 g (0.050 mole) of the m-fluoroiodosobenzene dichloride was carried out in a large mortar using the same method that has been previously employed. The desired material was isolated by filtration, and after washing successively with ice-cold water and ice-cold acetone, it was stored in a desiccator. The yield of white powder amounted to 8.5 g (71%).

3-Fluorodiphenyliodonium Bromide. A mixture of 20 ml of acetic anhydride in 100 ml of acetic acid was cooled to 0°, and 8.5 g (0.036 mole) of m-fluoroiodosobenzene was stirred into solution. About 20 ml (0.23 mole) of benzene was added, and then from a small dropping funnel there was added dropwise 8 ml of concentrated sulfuric acid; a clear, light-yellow solution resulted. After being stirred in the ice bath overnight, the solution was diluted with 150 ml of water and extracted once with ether to remove any m-fluoroiodobenzene. Addition of a strong solution of sodium bromide to the aqueous portion caused precipitation of a cream-colored solid which was filtered and washed with cold water, then with cold acetone.

The slightly moist material weighed 13.8 g and after standing for some time it began to acquire tinges of pink. Recrystallization from absolute methanol gave 5.8 g (54%) of white needles, mp 184-5°.

Anal. Calcd for $C_{12}H_9BrFI$: C, 38.0; H, 2.40; (Br+I) as Br: 47.5. Found: C, 38.18; H, 2.57; (Br+I) as Br, 46.80.

4-Fluorodiphenyliodonium Bromide. In a 500-ml, three-necked flask, fitted with electric stirrer, was placed 100 ml of concentrated sulfuric acid. The acid was cooled to near 0° in an ice bath and 25 g (0.113 mole) of p-fluoroiodobenzene was added with stirring. Then 30 g (0.131 mole) of ammonium persulfate was added portionwise; this resulted in a blood-red mixture. After the mixture had been stirred for another minute, there was added 43 g (0.552 mole) of benzene all at once. The suspension rapidly assumed a dirty-brown coloration. Stirring was continued at 0° for another 4.5 hours.

The brown suspension was poured with vigorous stirring onto crushed ice. Unconsumed benzene and tar were removed by ether extraction. The aqueous portion was then treated with Norite and after filtration a strong solution of sodium bromide was added with stirring to the light, pea-green solution. A milky-white precipitate formed and was allowed to settle overnight. The precipitate was filtered, washed successively with cold water, cold acetone and cold ether, and then stored in a desiccator to dry. The yield of white material was 12.6 g (29%), mp 192-198° (dec). After crystallization from absolute methanol, there resulted 9.8 g of material, mp 222-223°. A 0.5-g sample of this was recrystallized from absolute ethanol and then dried for analysis in an Abderhalden.

Anal. Calcd for $C_{12}H_9BrFI$: C, 38.0; H, 2.40; (Br+I) as Br: 47.5. Found: C, 38.20; H, 2.35; (Br+I) as Br: 47.20.

4-Fluorodiphenyliodonium Trifluoroacetate. A mixture of 3.50 g (9.2 mmole) of 4-fluorodiphenyliodonium bromide, 2.0 g (9.2 mmole) of silver trifluoroacetate and 150 ml of water was shaken in an Erlenmeyer flask wrapped with tin foil for 5 hours. The suspension was then filtered and the filtrate evaporated in a rotary evaporator at 50°. Last traces of water were removed by pumping in a desiccator for 2 hours. There was obtained 3.60 g (95%) of snow-white material, mp 163-168°. In the nmr spectrum of this material the aromatic protons were separated into three distinguishable groups centered at about δ 6.9, 7.8, and 8.7. A portion of this was recrystallized from benzene--acetone to give white material, mp 196-197°.

Anal. Calcd for $C_{14}H_9F_4IO_2$: C, 40.77; H, 2.21; I, 30.83. Found: C, 42.15; H, 2.11; I, 29.61.

3-Fluorodiphenyliodonium Trifluoroacetate. A mixture of 3.50 g (9.2 mmole) of 3-fluorodiphenyliodonium bromide, 2.04 g (9.2 mmole) of silver trifluoroacetate and 150 ml of water was shaken for 12 hours in a 500-ml flask. Silver bromide was then filtered off and the solution was taken to dryness in a rotary evaporator. After 2 hours of pumping in vacuo, the yield was determined to be 3.60 g (95%) of white crystals, mp 173-178°. Crystallization from benzene--acetone gave a white, fluffy solid, mp 205°.

Anal. Calcd for $C_{14}H_9F_4IO_2$: C, 40.77; H, 2.21; I, 30.83. Found: C, 40.80; H, 2.33; I, 29.06.

Fluorine nmr spectra of the two trifluoroacetates were taken in acetonitrile and dimethyl sulfoxide solutions; the latter material is a particularly good solvent for these salts. All solutions were approximately 10% by weight. Chemical shifts of these fluorides as well as of fluorobenzene were measured with respect to internal 1,2-difluorotetrachlorobenzene, which gives a sharp singlet 68.4 ppm upfield from external $CFCl_3$.

Cyclopropyllithium and Iodobenzene Dichloride. A 500-ml, three-necked, creased flask was fitted with reflux condenser, dropping funnel and high-speed stirrer. After the flask was flamed out under argon, there was added 100 ml of dry ether. A stream of argon was kept flowing through the system as 1.46 g (0.210 g-atom) of lithium wire was cut into pieces and added to the flask. Stirring was begun and a

solution of 12.1 g (0.100 mole) of cyclopropyl bromide in 200 ml of ether was added. The contents were maintained at 0-5° for the next 4 hours; during this time lithium bromide precipitated and the suspension turned creamy-pink. The suspension was then cooled to about -55° and over a period of one hour there was added 27.5 g (0.100 mole) of iodobenzene dichloride; stirring was continued for 5 more hours.

The creamy sludge was filtered and washed with cold water. This dissolved everything except a small amount of unchanged dichloride. To the aqueous layer of the filtrate was added a strong solution of sodium bromide; no precipitation occurred indicating the absence of iodonium ions.

The ether layer was concentrated somewhat, dried over sodium sulfate, and analyzed on an SE-30 column at 185°. The results of the VPC analysis showed cyclopropyl chloride, cyclopropyl bromide, cyclopropyl iodide, chlorobenzene, bromobenzene, and iodobenzene to be present according to the observed retention times. No new peaks appeared when the temperature of the column was increased to 210°. Cyclopropylbenzene was not present in the mixture.

Iodocyclopropane Dichloride and Phenyllithium. Phenyllithium was prepared in a 500-ml, three-necked, creased flask from 8.0 g (0.051 mole) of bromobenzene, 0.9 g (0.130 g-atom) of lithium wire and 250 ml of ether. The mixture was agitated with a high-speed stirrer at 0° for 5 hours. The dichloride (10.2 g, 0.043 mole) was then added in portions to the stirred phenyllithium while a temperature of -50° was maintained with a dry ice--acetone bath. After the addition of a few

portions of the dichloride, the suspension assumed a green coloration, later turning to orange after more dichloride was added. The suspension was then stirred overnight and the bath was allowed to come to room temperature.

The suspension was filtered and the filtrate washed successively with aqueous sodium bisulfite, sodium carbonate and saturated sodium chloride solutions. The residue from the above filtration dissolved completely when washed with cold water. Addition of aqueous sodium bromide to the aqueous rinse produced no precipitate. The ether solution obtained from the reaction was examined without further concentration on an SE-30 silicon oil column at 160°. The chromatogram contained many peaks; identification was done by a comparison of retention times with authentic materials. In addition to some unconsumed bromobenzene, there were present benzene, chlorobenzene, and iodobenzene. No cyclopropyl iodide was present, and at most, only a trace of cyclopropyl chloride was present. Two additional peaks were present which were not identified.

When an analogous reaction was carried out between phenyllithium and 1-iodoapocamphane dichloride, similar results were obtained. No iodonium salt could be isolated; benzene, bromobenzene, chlorobenzene, and iodobenzene were all present in the ether solution. The fate of the apocamphane skeleton was not pursued.

Triptycyllithium and Iodobenzene Dichloride. A 500-ml, three-necked flask was fitted with magnetic stirrer, gas inlet tube, a rubber serum cap, and in the center neck a curved tube with a volume of about 50 ml.

The system was flamed out under argon and in the curved tube was placed 3.25 g (11.8 mmole) of iodobenzene dichloride which had previously been pumped on in vacuo for several hours. By means of a pipette 95 ml of dry benzene and 225 ml of dry ether were placed in the flask and 4.00 g (12 mmole) of 9-bromotriptycene was added to this. After solution was effected, the whole was cooled to -50° and with stirring under argon there was added from a syringe over a period of 45 minutes 9.5 ml (15.2 mmole) of 1.6 M n-butyllithium in hexane. Stirring was continued for 30 minutes at -50° and then for one hour at -70°. By tilting the curved tube upward the iodobenzene dichloride was added in portions over an hour, followed by stirring for 10 more hours. The apparatus was then capped and allowed to sit in the freezer for 2 days.

The white, precipitated solid was filtered and washed with cold water. The isolated solid amounted to 0.47 g, mp 253-255°; its infrared spectrum showed it to be unchanged 9-bromotriptycene. When potassium iodide solution was added to the above aqueous wash there precipitated 0.1 g of a white solid, mp 178°. This was shown to be diphenyliodonium iodide. The ether--benzene filtrate from above was concentrated and separated into a solid residue and a clear liquid. The solid had mp 209-242° and from the infrared spectrum was judged to be a mixture of 9-bromotriptycene and 9-iodotriptycene. The clear liquid portion was examined by vapor-phase chromatography on a silicon oil column at 170°. The following were shown to be present: ether, hexane, benzene, n-butyl bromide, chlorobenzene and

iodobenzene; the latter two were present in roughly equal amounts.

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FLUORINE-19 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF CYCLIC AND BICYCLIC SYSTEMS

FLUORINE-19 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF CYCLIC AND BICYCLIC SYSTEMS

I. Background and Introduction

Fluorine-19 nuclear magnetic resonance spectroscopy began in 1950 when Dickinson (1) and Gutowsky and Hoffman (2) independently observed resonance signals in a number of fluorine compounds. These authors observed that chemical-shift differences between compounds were much larger than proton chemical-shift differences in analogous or similar compounds. Table 1 presents some representative data to illustrate this point.

Table 1. Comparative ^{19}F and ^{1}H Chemical Shift Data

Compound	^{19}F Shift (ppm)[a]	^{1}H Shift (ppm)[b]	Compound
F_2	0	0	H_2
NF_3	285.0	4.25	NH_3
PF_3	463.7	5.68	PH_3
CF_4	491.0	4.20	CH_4
SiF_4	598.9	7.20	SiH_4

[a] Data from reference 2.

[b] Data from W. G. Schneider, H. J. Bernstein and J. A. Pople, J. Chem. Phys., 28, 601 (1958).

In the early development of the theory of nuclear magnetic shielding, chemical-shift differences between different kinds of nuclei in atomic systems were accounted for by means of the Lamb equation, shown below (3).

$$\sigma = \frac{4\pi e^2}{3 m c^2} \int_0^\infty r \rho(r)\, dr . \qquad \text{(II-1)}$$

Using the best Hartree-type wavefunctions which were available at the time, Dickinson was able to estimate the magnitude of the nuclear shielding for different kinds of atoms (4). Gradually, workers realized that the Lamb equation was insufficient to account for the significant differences in shielding of a given type of nucleus in different compounds. The necessary theoretical formalism was supplied by Ramsey, who developed an expression for the shielding parameter using second-order perturbation theory (5). According to this treatment, the shielding parameter is comprised of a diamagnetic contribution and a paramagnetic contribution, analogous to the Van Vleck theory of magnetic susceptibility (6). Shortly after Ramsey's treatment appeared, Saika and Slichter showed how this formalism could satisfactorily account for the large observed chemical-shift difference between fluorine and hydrogen fluoride (7).

The Ramsey equation has rarely been used directly for the computation of a shielding parameter, mainly for the reason that it requires a detailed knowledge of both excited state molecular eigenfunctions and eigenvalues. Consequently, different approaches to the problem have

been pursued by various workers. Stephen (8) and several other investigators (9-13) have applied the variation method as a means of calculating the shielding parameter. In Stephen's treatment a trial function of the form

$$\psi = \psi_0 (1 + \vec{H} \cdot \vec{g} + \vec{\mu} \cdot \vec{f}) \qquad \text{(II-2)}$$

is used in the minimization of the functional

$$L(\phi) = \frac{\langle \psi | \hat{\mathcal{H}} | \psi \rangle}{\langle \psi | \psi \rangle}$$

where ψ_0 is the ground state (unperturbed) wavefunction, and $\underline{g}$ and $\underline{f}$ are unknown functions. Since the energy of interaction between the atom N of interest and the applied magnetic field is formulated as

$$E'_N = \sigma_N \vec{\mu} \cdot \vec{H}, \qquad \text{(II-3)}$$

one simply picks out those terms arising in the minimization which are linear in μH. All operations are done solely with a ground-state molecular wavefunction.

Another alternative to direct application of the Ramsey equation has been developed by Pople (14-17) and by Karplus and Das (18). Basically, what these authors do is to make the LCAO approximation and reduce the Ramsey equation to an expression containing molecular orbital coefficients and eigenvalues. Several drastic mathematical simplifications must be made in order to give a tractable expression.

Specific applications to fluorine shielding in conjugated fluorine compounds and to xenon shielding in the xenon fluorides have been made by Prosser and Goodman (19) and Jameson and Gutowsky (20), respectively.

Although it has generally been difficult to extract much chemical information from the Ramsey equation, it has been possible to formulate some reasonable working rules correlating shielding and certain empirical parameters. Gutowsky and Hoffman (2a) noted a fair correlation between the fluorine chemical shifts of several fluorine compounds and the electronegativity of the central atom to which the fluorine is bonded. The figure below summarizes some of the authors' data.

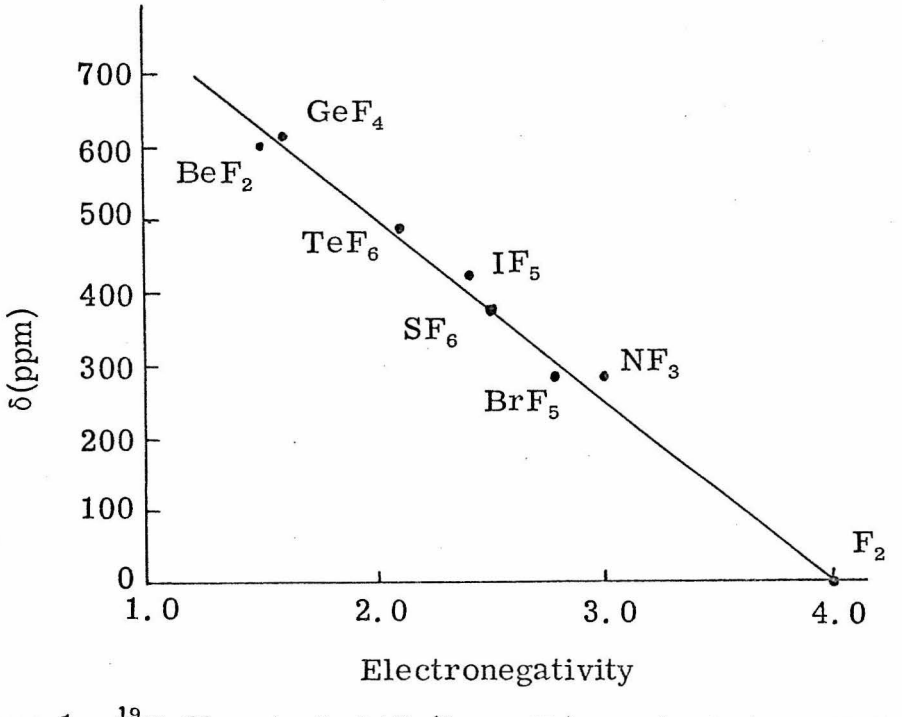


Figure 1. ^{19}F Chemical shift (from F_2) vs electronegativity

In the more restricted set of compounds, the meta-substituted fluorobenzenes, Taft (21) finds an excellent correlation between the fluorine chemical shifts and the σ_I-inductive parameters, previously obtained from reactivities (22). The straight line shown in the graph below corresponds to the linear equation

$$\delta_m = -5.83\,\sigma_I + 0.20. \qquad \text{(II-4)}$$

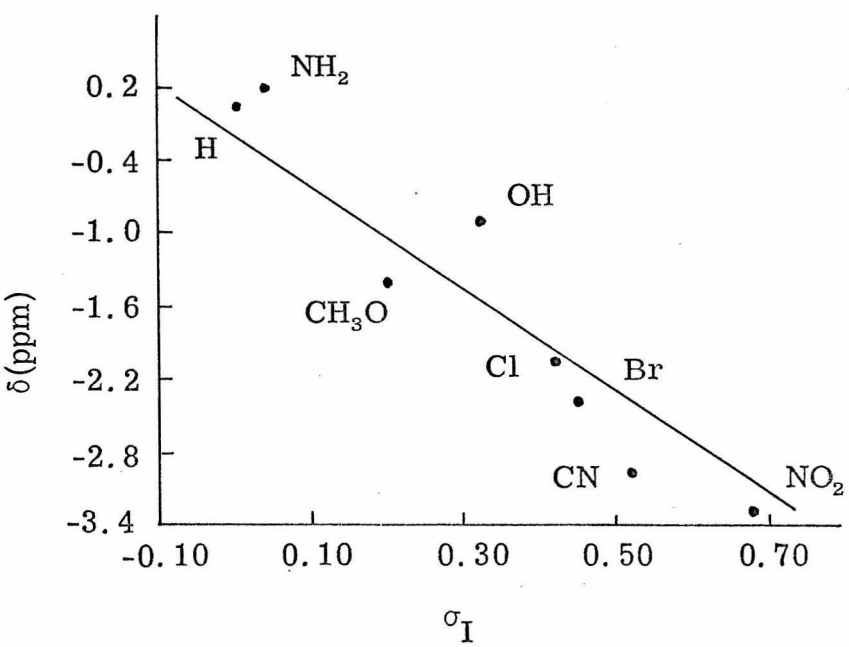


Figure 2. ^{19}F Chemical shift (from C_6H_5F) vs σ_I for some m-fluorobenzenes

Similarly, it was found by Bothner-By and Glick that chemical-shift data for the para proton of monosubstituted benzenes could be linearly correlated with the Hammett σ values (23).

Finally, for nuclei other than hydrogen and fluorine, it has been found that carbon-13 chemical shifts in CH_3–X compounds can be correlated with the electronegativities of the X atoms (24a), although Bucci finds that the correlation can be improved by making the chemical shift a linear function of both electronegativity and the number of lone pairs on X (24b). The physical significance of this additional term is difficult to ascertain. The cobalt-59 chemical shifts in a series of cobalt complexes correlate well with the wavelength of the lowest-frequency optical-absorption maximum (25a). Similar tendencies were found for N-15 chemical shifts (25b) and for O-17 chemical shifts (25c).

Thus, even though the idealistic goal of an a priori correlation of nuclear shielding (or any other nmr parameter) with chemical structure is still a long way off, much useful information can be gained from a more empirical approach. The approach taken in the present work lies between these two extremes. In order to provide a balanced introduction to the problem at hand, it is desirable to present a brief résumé of the theoretical background of nuclear shielding.

II. Theoretical Prelude

At any point in a region where electromagnetic radiation exists we may associate an electric field vector $\vec{E}$ and a magnetic field vector $\vec{H}$.* A particle of mass $\underline{m}$ and charge $\underline{e}$ moving with a velocity $\vec{v}$ in this field will experience a force

$$\vec{F} = e\left(\vec{E} + \frac{1}{c}[\vec{v} \times \vec{H}]\right). \qquad \text{(II-5)}$$

Physicists have found it more useful to work with a vector potential $\vec{A}$ and a scalar potential V, defined as

$$\vec{H} = \text{curl } \vec{A} \qquad \text{(II-6)}$$

$$\vec{E} = -\frac{1}{c}\frac{\partial}{\partial t}\vec{A} - \nabla V, \qquad \text{(II-7)}$$

rather than with $\vec{H}$ and $\vec{E}$. Newton's second law may thus be written (for the x-coordinate)

$$m\frac{d^2x}{dt^2} = -e\frac{\partial V}{\partial x} - \frac{e}{c}\frac{\partial A_x}{\partial t} + \frac{e}{c}\left[\frac{dy}{dt}\left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right) + \frac{dz}{dt}\left(\frac{\partial A_z}{\partial x} - \frac{\partial A_x}{\partial z}\right)\right]. \qquad \text{(II-8)}$$

Since the Lagrangian form of Newton's second law of motion is

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} - \frac{\partial L}{dx} = O, \qquad (L = T\text{-}U;\ \dot{x} = \frac{dx}{dt})$$

---

* In some books the symbol $\vec{B}$ is used, reserving $\vec{H}$ for the magnetic intensity vector.

it is not difficult to see that equation (II-8) derives from the Lagrangian

$$L = \frac{m}{2}\left[\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2\right] + \frac{e}{c}\left(A_x\frac{dx}{dt} + A_y\frac{dy}{dt} + A_z\frac{dz}{dt}\right) - eV. \qquad \text{(II-9)}$$

Linear momentum is $\frac{\partial L}{\partial x}$ (for the x-component); this works out to be

$$p_x = m\frac{dx}{dt} + \frac{e}{c}A_x. \qquad \text{(II-10)}$$

Thus, the velocity is no longer $p_x m^{-1}$, but rather $(p_x - \frac{e}{c}A_x)/m$. At this point, Carrington and McLachlan follow a derivation which is somewhat less than satisfying and which also uses a form of the vector potential different from what we shall employ (26). For our vector potential we shall take

$$\vec{A} = \frac{1}{2}(\vec{H}\times\vec{r}) + r^{-3}(\vec{\mu}\times\vec{r}) \qquad \text{(II-11)}$$

where the first term relates to the applied field and the second term to the dipolar field created by the nucleus with a magnetic dipole moment $\vec{\mu}$.

Quantum mechanically, one now has to replace classical momentum by the operator $-i\hbar\nabla$, so that the Hamiltonian for the system is

$$\hat{\mathcal{H}} = (-i\hbar\nabla + \frac{e}{c}\vec{A})^2/2m + U$$

$$= \frac{-\hbar^2}{2m}\nabla^2 - \frac{ie\hbar}{mc}[\vec{A}\cdot\nabla + \operatorname{div}\vec{A}] + \frac{e^2}{2mc^2}\vec{A}^2 + U \qquad \text{(II-12)}$$

It is customary to set $\operatorname{div}\vec{A}$ equal to zero. The argument for this is that a vector is not specified completely by giving only its curl; hence, we are free to impose a restriction on its divergence which will simplify the problem at hand. The Coulomb gauge (27) is usually invoked when discrete charges are not present; as a result, one of the Maxwell equations is transformed directly into Poisson's equation.*

After substituting equation (II-11) into equation (II-12), the Hamiltonian becomes

$$\hat{\mathcal{H}} = p^2/2m + U$$

$$= \frac{1}{2m}\left[-i\hbar\nabla + \frac{e}{2c}(\vec{H}\times\vec{r}) + \frac{e}{c}r^{-3}(\vec{\mu}\times\vec{r})\right]^2 + U$$

---

*In the absence of a dielectric the first Maxwell equation may be written $\operatorname{div}\vec{E} = 4\pi\rho$. For the time-dependent case, $\vec{E} = -\overrightarrow{\operatorname{grad}}\,\phi - \frac{1}{c}\times\frac{\partial\vec{A}}{\partial t}$. Hence, one has $\nabla^2\phi + \frac{1}{c}\frac{\partial}{\partial t}\operatorname{div}\vec{A} = -4\pi\rho$ which becomes Poisson's equation if $\operatorname{div}\vec{A} = 0$. Note that for $\vec{A} = \frac{1}{2}\vec{H}\times\vec{r}$ one has $\operatorname{div}\vec{A} = \frac{1}{2}[\vec{r}\cdot\operatorname{curl}\vec{H} - \vec{H}\cdot\operatorname{curl}\vec{r}] = \frac{1}{2}[-2\vec{H}\cdot\operatorname{curl}\vec{r}] = 0$ for $r = \vec{i}x + \vec{j}y + \vec{k}z$.

$$\hat{\mathcal{H}} = \left[\frac{-\hbar^2}{2m}\nabla^2 + U\right] + \left[\frac{e\hbar}{2imc}\vec{H}\cdot(\vec{r}\times\nabla) + \frac{e\hbar}{imcr^3}\vec{\mu}\cdot(\vec{r}\times\nabla)\right]$$

$$+ \frac{e^2}{8mc^2}\left[\vec{H}\times\vec{r} + 2r^{-3}(\vec{\mu}\times\vec{r})\right]^2$$

$$= \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2$$

The last two terms constitute the perturbation contribution to the Hamiltonian. Since first-order perturbation theory applied to the $\hat{\mathcal{H}}_1$ term will not yield any terms that are linear in the product μH, we go next to second-order perturbation theory. The well-known, second-order correction to the energy is (28):

$$E^{(2)} = -\sum_n{}' \frac{\langle n|\hat{\mathcal{H}}'|O\rangle\langle O|\hat{\mathcal{H}}'|n\rangle}{E_n - E_O} \qquad \text{(II-13)}$$

Hence, the total correction to the energy is simply

$$E' = \langle O|\hat{\mathcal{H}}_2|O\rangle - \sum_n{}' \frac{\langle n|\hat{\mathcal{H}}_1|O\rangle\langle O|\hat{\mathcal{H}}_1|n\rangle}{E_n - E_O}$$

$$= \frac{e^2}{2mc^2}\langle O|(\vec{\mu}\times\vec{r})\cdot(\vec{H}\times\vec{r})r^{-3}|O\rangle +$$

$$\sum_n{}' \frac{\langle n|\frac{ie\hbar}{2mc}\vec{H}\cdot(\vec{r}\times\nabla)|O\rangle\langle O|\frac{ie\hbar}{mcr^3}\vec{\mu}\cdot(\vec{r}\times\nabla)|n\rangle}{E_n - E_O} +$$

$$\sum_n{}' \frac{\langle n|\frac{ie\hbar}{mcr^3}\vec{\mu}\cdot(\vec{r}\times\nabla)|O\rangle\langle O|\frac{ie\hbar}{2mc}\vec{H}\cdot(\vec{r}\times\nabla)|n\rangle}{E_n - E_o}$$

$$= \frac{e^2}{2mc^2}\langle O|[(\vec{\mu}\cdot\vec{H})r^2 - (\vec{\mu}\cdot\vec{r})(\vec{r}\cdot\vec{H})]/r^3|O\rangle - 4\,\mathrm{Re}\times$$

$$\sum_n{}' \frac{\langle n|\frac{\vec{\mu}\cdot\vec{M}}{r^3}|O\rangle\langle O|\vec{H}\cdot\vec{M}|n\rangle}{E_n - E_o} \qquad \text{(II-14)}$$

where $\vec{M} = \frac{ie\hbar}{2mc}\vec{r}\times\nabla$, and where use has been made of the vector identity

$$(\vec{A}\times\vec{B})\cdot(\vec{C}\times\vec{D}) = (\vec{A}\cdot\vec{C})(\vec{B}\cdot\vec{D}) - (\vec{A}\cdot\vec{D})(\vec{B}\cdot\vec{C}).$$

The shielding parameter is defined to be a tensor (having nine components) with the property

$$\boxed{E' = \mu\cdot\underset{\sim}{\sigma}\cdot H} \qquad \text{(II-15)}$$

Thus, μ and H must be divided out of equation (II-14) in such a way as to leave the result a tensor. For example, the zz-component of the first term of the shielding will be

$$\sigma_{zz} = \frac{e^2}{2mc^2}\langle O|[(\mu_z H_z)r^2 - (\mu_z z)(zH_z)]\,r^{-3}|O\rangle/\mu_z H_z \qquad \text{(II-16)}$$

$$= \frac{e^2}{2mc^2}\langle O|\frac{x^2+y^2}{r^3}|O\rangle$$

The language of dyadics is used to formulate the required division (29).

The final result for the shielding tensor is

$$\underset{\sim}{\sigma}_N = \frac{e^2}{2mc^2} \langle O | [\underset{\sim}{I}(\vec{r}\cdot\vec{r}) - \vec{r}\vec{r}] \; r^{-3} | O \rangle - 4\,\mathrm{Re} \sum_n{}' \frac{\langle n | \frac{\vec{M}}{r^3} | O \rangle \langle O | \vec{M} | n \rangle}{E_n - E_o} \tag{II-17}$$

The meaning of $\underset{\sim}{I}$, the idemfactor, is the matrix operator

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

so that $\underset{\sim}{I}(\vec{r}\cdot\vec{r})$ is equal to

$$\underset{\sim}{I}(\vec{r}\cdot\vec{r}) = \underset{\sim}{I}(x^2+y^2+z^2) \equiv \begin{pmatrix} x^2+y^2+z^2 & 0 & 0 \\ 0 & x^2+y^2+z^2 & 0 \\ 0 & 0 & x^2+y^2+z^2 \end{pmatrix}. \tag{II-18}$$

In a similar manner, the dyadic $\vec{r}\vec{r}$ is the matrix operator

$$\vec{r}\vec{r} \equiv \begin{pmatrix} x^2 & xy & xz \\ xy & y^2 & yz \\ xz & yz & z^2 \end{pmatrix}. \tag{II-19}$$

One final point: equation (II-17) is applicable to a one-electron system. For the general case where there are k electrons, the shielding tensor becomes

$$\underset{\sim}{\sigma}_N = \frac{e^2}{2mc^2} \langle O| \sum_{j=1}^{k} [\underset{\sim}{I}(\vec{r}_j \cdot \vec{r}_j) - \vec{r}_j \vec{r}_j] r_j^{-3} |O\rangle - 4\,\mathrm{Re} \sum_{n}' \frac{\langle n| \sum_{j=1}^{k} \frac{\vec{M}_j}{r_j^3} |O\rangle \langle O| \sum_{j=1}^{k} \vec{M}_j |n\rangle}{E_n - E_o} \qquad \text{(II-20)}$$

The equation thus obtained (Ramsey's equation) is seen to consist of a term that involves the excited-state wavefunctions (the paramagnetic term). This complex term is extremely difficult to evaluate since it involves hard-to-get functions, and also an infinite series of indeterminate form. In theory, the continuum should also be included in the paramagnetic term, but this does not seem to have been investigated in detail, except for one report by Snyder and Parr (30).

For proton shielding, the diamagnetic term dominates, although when considering differences in the shielding, the paramagnetic term should not be neglected. Hence, good wavefunctions are needed in order to avoid large errors when taking the difference. The dominating factor in proton shifts is the distance of the electrons from the nucleus of interest, that is, $1/r_j$. Electron-withdrawing groups (-I) would tend to increase r_j and therefore produce shifts to lower field. The data in the table below support this idea. Although one is

prevented in the usual sense of the meaning from actually measuring absolute values of σ, Ramsey has recently done an elegant determination of the ratio of the electron to the proton g factors in atomic hydrogen, which after comparison with previous data for $g_j(H)/g_p(H_2O)$, permits an absolute value to be assigned to the shielding in water (31). The numbers in the last column of Table 2 are therefore "experimental" values based upon this determination. Crude molecular orbital calculations of charge densities in molecules support the correlation of chemical shift with ^1H charge density (32, 33).

Table 2. Shielding Data for Various Hydrides, H_nX

Compound	Electronegativity of X	σ_d(ppm)	σ_p(ppm)	σ(ppm)	σ(expt.)
HF[a]	4.0	34.7	-6.8	27.9	24.2
HCl[a]	3.0	38.3	-4.2	34.1	27.13
HBr[a]	2.8	40.3	-3.2	37.1	30.93
HI[a]	2.5	43.4	-1.7	42.7	39.83
H_2O[b]	3.5			27.9	25.98
H_2S[b]	2.5			29.2	26.50
H_2Se[b]	2.4			28.9	30.0

[a] Calculations of Hameka: H. F. Hameka, Mol. Phys., 2, 64 (1959).

[b] Calculations of Fixman: reference 11.

For elements of the second row, where now there are p-electrons available, chemical shifts tend to be dominated by fluctuations in the paramagnetic term. This point is difficult to prove by means of complete calculations because of the intractability of the second term in Ramsey's equation. Calculations of a more approximate nature reveal only small changes in the diamagnetic term, so that the large observed shifts must be due to the paramagnetic contribution.

It should be mentioned that the particular form of equation (II-20) is a consequence of the fact that the origin of the vector potential $\vec{A}$ had been taken as being at the nucleus of interest. One could equally well have used the vector potential $\vec{A}' = 1/2\ \vec{H} \times \vec{r} + \frac{\vec{\mu} \times \vec{r}}{r^3} + \overrightarrow{\text{grad}}\, f$ instead, where f is some arbitrary function of the coordinates. This is equivalent to simply working in a different coordinate system; however, the fundamental regularity of Nature leads us to suppose that observable properties should be independent of the choice of coordinate system.

Let ψ be an exact solution of

$$\hat{\mathcal{H}}\psi = E\psi \qquad \text{(II-21)}$$

using the vector potential $\vec{A}$ and the Hamiltonian

$$\hat{\mathcal{H}} = \frac{1}{2m}\left(\vec{p} - \frac{e}{c}\vec{A}\right) + V.$$

We now make a gauge transformation

$$\vec{A}' = \vec{A} + \overrightarrow{\text{grad}}\, f \qquad \text{(II-22)}$$

giving a new Hamiltonian and therefore a new wavefunction. The electron no longer has linear momentum $\vec{p} - \frac{e}{c}\vec{A}$, but rather $\vec{p} - \frac{e}{c}\vec{A} - \frac{e}{c}\overrightarrow{\text{grad}}\, f$. Assume a new wavefunction of the form

$$\psi' = \psi e^{i0f}$$

where 0 is a constant. The expectation value of the new linear momentum is now

$$\langle p' \rangle = \langle \psi e^{i0f} | \vec{p} - \frac{e}{c}\vec{A} - \frac{e}{c}\overrightarrow{\text{grad}}\, f | \psi e^{i0f} \rangle$$

$$= \langle \psi e^{i0f} | \vec{p} | \psi e^{i0f} \rangle - e^{-i0f} \langle \psi | \frac{e}{c}\vec{A} | \psi \rangle e^{i0f}$$

$$- e^{-i0f} \langle \psi | \frac{e}{c}\overrightarrow{\text{grad}}\, f | \psi \rangle e^{i0f}$$

$$= -i\hbar \langle \psi e^{i0f} | e^{i0f} \overrightarrow{\text{grad}}\, \psi + \psi \overrightarrow{\text{grad}}\, e^{i0f} \rangle -$$

$$\langle \psi | \frac{e}{c}\vec{A} | \psi \rangle - \langle \psi | \frac{e}{c}\overrightarrow{\text{grad}}\, f | \psi \rangle$$

$$= -i\hbar \langle \psi | \overrightarrow{\text{grad}}\, \psi \rangle - i\hbar \langle \psi e^{i0f} | i0\psi e^{i0f} \overrightarrow{\text{grad}}\, f \rangle$$

$$- \langle \psi | \frac{e}{c}\vec{A} | \psi \rangle - \langle \psi | \frac{e}{c}\overrightarrow{\text{grad}}\, f | \psi \rangle$$

$$= \langle\psi \mid \vec{p}\mid\psi\rangle + \hbar 0\langle\psi \mid \vec{\text{grad}}\, f\mid\psi\rangle -$$

$$\langle\psi \mid \frac{e}{c}\vec{A}\mid\psi\rangle - \frac{e}{c}\langle\psi \mid \vec{\text{grad}}\, f\mid\psi\rangle$$

$$= \langle p\rangle + \hbar 0\langle\psi \mid \vec{\text{grad}}\, f\mid\psi\rangle - \frac{e}{c}\langle\psi \mid \vec{\text{grad}}\, f\mid\psi\rangle . \qquad \text{(II-23)}$$

Equation (II-23) simplifies considerably if

$$0 = \frac{e}{\hbar c} = \frac{\alpha}{e}.$$

Similar invariance can easily be shown for other operators. In practice one never has exact wavefunctions, so that the choice of gauge is usually a problem that must be faced. In a recent paper by Hegstrom and Lipscomb (34), the following results emerged from a calculation on $^{11}B\ ^{19}F$:

Table 3. Calculated Shielding in $^{11}B^{19}F$

Gauge origin at	F(ppm)	B(ppm)
(B)	202.71	268.35
(B)	-120.60	-184.70
(B)	82.11	83.64
(F)	507.77	470.37
(F)	-264.36	-212.86
(F)	243.42	257.51

Although large differences exist for each individual term, these are largely canceled when the total shielding is obtained. Data similar to these are not available for polyatomic molecules.

To be able to apply the Ramsey formalism to interesting molecules one must introduce further approximations. This section will be closed by discussing three approaches which have been taken by Ramsey (5), McConnell (38) and Pople (15), successively.

Approximation 1

Suppose one has the expression

$$\sum_{n'''} \langle n' | \hat{L} | n''' \rangle \langle n''' | \hat{M} | n'' \rangle$$

which may also be written as

$$\sum \int\int g^*_{n'}(q)\, \hat{L}\,(p, q)\, g_{n'''}(q)\, g^*_{n'''}(q')\, \hat{M}\,(p', q')\, g_{n''}(q')\, dq\, dq' \qquad (II\text{-}24)$$

The functions $g_n(q)$ form a complete orthogonal set, so that any other function of q, F (q), can then be expanded in terms of the g_n's:

$$F(q) = \sum_n A_n\, g_n(q)$$

where $A_n = \int F(q')\, g^*_n(q')\, dq'$ (35).

Then it follows that

$$F(q) = \sum_n \int F(q')\, g^*_n(q')\, g_n(q)\, dq' \qquad (II\text{-}25)$$

This type of term appears in (II-24) as

$$\sum_{n'''} \int \hat{M}(p', q')\, g^*_{n'''}(q')\, g_{n'''}(q)\, dq' ,$$

so that it is easily seen that (II-24) simplifies to

$$\int g^*_{n'}(q)\, \hat{L}(p, q)\, \hat{M}(p', q')\, g_{n'''}(q')\, dq ,$$

or equivalently to $\langle n' \left| \hat{L}\hat{M} \right| n'' \rangle$.

Using this result one can simplify the paramagnetic term of equation (II-20) to

$$\underset{\sim}{\sigma}_p = \frac{-4}{\Delta E} \langle O \left| \sum_{j,k} \hat{M}_j\, \hat{M}_k\, r_j^{-3} \right| O \rangle . \qquad \text{(II-26)}$$

The effect of rapid rotation is to make the operator $\hat{M}_{zj} \cdot \hat{M}_{zk}$ equivalent to $\hat{M}_{xj} \cdot \hat{M}_{xk}$ and $\hat{M}_{yj} \cdot \hat{M}_{yk}$; hence, the factor 1/3 must be affixed to the above expression. The simplified shielding expression is, therefore,

$$\boxed{\sigma_N = \frac{e^2}{3mc^2} \left[\langle O \left| \sum_j \sum_k \left[r_j^{-1} - 4 \left(\frac{mc^2}{e^2}\right) \left(\frac{1}{\Delta E}\right) r_j^{-3}\, \hat{M}_j \cdot \hat{M}_k \right] \right| O \rangle \right]} \qquad \text{(II-27)}$$

This expression now requires knowledge of only the ground-state wavefunction, paid for at the expense of introducing the questionable "average energy of excitation." McLachlan (36) and Alexander (37) have commented on the validity of the average-energy approximation;

the approximation may be justified for cases where a localized bond description of the molecule is accurate.

Approximation 2

In this approximate treatment, due to H. M. McConnell (38), we derive the contribution to the shielding of nucleus N due to a group G in the molecule. It is assumed that G is essentially isolated from N so that electrons in G move in molecular orbitals which have a very low probability density about N; the same is assumed to be true for the excited states of G. A wavefunction for the molecule can then be factored

$$\psi_n = \psi_n^G \psi_{rest},$$

and substitution into equation (II-20) gives for the contribution to the shielding by group G

$$\underset{\sim}{\sigma}_N^G = \frac{e^2}{2mc^2} \langle OG | \sum_j [\underset{\sim}{I}(\vec{r}_j \cdot \vec{r}_j) - \vec{r}_j \vec{r}_j] r_j^{-3} | OG \rangle - 4\,\mathrm{Re} \sum_n' \frac{\langle nG | \sum_{j=1}^{k} \frac{\vec{M}_j}{r_j^3} | OG \rangle \langle OG | \sum_{j=1}^{k} \vec{M}_j | nG \rangle}{E_n - E_o} \qquad \text{(II-28)}$$

The assumption that G is isolated from N allows one to go to a new origin in G

$$\vec{r}_j^{\,G} = \vec{r}_j - \vec{R}$$

$$\hat{M}_j^{\,G} = \hat{M}_j - \frac{e}{2mc}\,\vec{R}\times\vec{p}_j \qquad |\vec{R}| \gg |\vec{r}_j^{\,G}|$$

and write by means of the binomial theorem

$$r_j^{-3} \sim R^{-3} + 3(\vec{r}_j^{\,G}\cdot\vec{R})/R^5 - \frac{3}{2}(r_j^{\,G})^2/R^5 + \frac{15}{2}(\vec{r}_j^{\,G}\cdot\vec{R})^2/R^7. \quad \text{(II-29)}$$

Substitution of these expressions into equation (II-28) gives to third order in R^{-1}:

$$\underset{\sim}{\sigma}_N^{\,G} = \frac{\underset{\sim}{\chi}^G}{R^3} - \frac{3\,\underset{\sim}{\chi}^G\cdot\vec{R}\,\vec{R}}{R^5} \quad \text{(II-30)}$$

where $\underset{\sim}{\chi}^G$ is the susceptibility tensor

$$\underset{\sim}{\chi}^G = -\frac{e^2}{4mc^2}\langle OG|\sum_j[\underset{\sim}{I}(\vec{r}_j^{\,G}\cdot\vec{r}_j^{\,G}) - \vec{r}_j^{\,G}\vec{r}_j^{\,G}](r_j^{\,G})^{-3}|OG\rangle + \quad \text{(II-31)}$$

$$2\,\mathrm{Re}\sum_{n'}\frac{\langle nG|\sum_{j=1}^{k}\vec{M}_j^{\,G}|OG\rangle\langle OG|\sum_{j=1}^{k}\vec{M}_j^{\,G}|nG\rangle}{E_n - E_0}$$

To finally simplify equation (II-30) we rewrite the numerator as

$$\underset{\sim}{\chi}^G R^2 - 3\vec{R}\cdot\underset{\sim}{\chi}^G\cdot\vec{R}$$

and call the G-symmetry axis the z-axis. Then the xx-, yy-, and zz-components of $\underset{\sim}{\sigma}_N^{\,G}$ can be written

$$\sigma_{xx}^{G} = \frac{\chi_{\perp}^{G}(y^2 + z^2 - 2x^2)}{R^5}$$

$$\sigma_{yy}^{G} = \frac{\chi_{\perp}^{G}(x^2 + z^2 - 2y^2)}{R^5}$$

$$\sigma_{zz}^{G} = \frac{\chi_{\parallel}^{G}(x^2 + y^2 - 2z^2)}{R^5}$$

where $\chi_{\parallel}^{G}$ and $\chi_{\perp}^{G}$ are the susceptibilities parallel and perpendicular to the z-axis. Since experimentally one measures an averaged σ, we then have

$$\sigma^{G} = \frac{1}{3}(\sigma_{xx}^{G} + \sigma_{yy}^{G} + \sigma_{zz}^{G})$$

$$= \frac{\Delta\chi^{G}}{3R^3}(1 - 3z^2/R^2), \qquad \Delta\chi^{G} = \chi_{\parallel}^{G} - \chi_{\perp}^{G}.$$

We note that z/R is actually the cosine of the angle between R and the z-axis. Averaging over all such orientations gives finally

$$\langle \sigma_{N}^{G} \rangle = \frac{\Delta\chi^{G}}{3R^3N} \langle 1 - 3\cos^2\theta \rangle \qquad \text{(II-33)}$$

where χ^{G} is now a <u>molar</u> susceptibility scalar and N is Avogadro's number. For a rigid molecule this averaging process would be unnecessary.

Approximation 3

Pople has derived an expression for the shielding tensor in the framework of molecular orbital theory. His rather abstruse derivation actually begins at the same point as does Ramsey's treatment; in this section we shall show that Pople's formula can be derived directly from the Ramsey equation. The demonstration breaks down into two parts: computation of the diamagnetic term and the paramagnetic term.

From equation (II-27) one sees that the "experimentally observed" diamagnetic term of the shielding parameter is

$$\sigma = \frac{e^2}{3mc^2} \langle O| \sum_k \frac{1}{r_n} |O\rangle \qquad \text{(II-34)}$$

where r_k is the distance of the k'th electron from the nucleus of interest. For a closed shell of 2N electrons one can express the wavefunction as a Slater determinant of one-electron spinorbitals.

$$\psi(1, 2, \cdots, N) = \sqrt{1/(2N)!} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(2)\alpha(2) \cdots \phi_1(2N)\alpha(2N) \\ \phi_1(1)\beta(1) & \phi_1(2)\beta(2) \cdots \phi_1(2N)\beta(2N) \\ \phi_2(1)\alpha(1) & \phi_2(2)\beta(2) \cdots \phi_2(2N)\beta(2N) \\ \vdots & \\ \phi_N(1)\beta(1) & \phi_N(2)\beta(2) \cdots \phi_N(2N)\beta(2N) \end{vmatrix}$$

(II-35)

The operator $\frac{1}{r_k}$ is a one-electron operator; according to Slater's rules for calculating the matrix elements of one-electron operators between two determinants, if $\hat{O}_j$ is such an operator, then

$$I = \int \psi_A^* \sum_j \hat{O}_j \psi_B \, d\tau_1 \, d\tau_2 \cdots d\tau_{2N}$$

$$= \sum_j \int \phi_j \hat{O} \phi_j \, d\tau$$

when the determinants are identical (39, 40). The diamagnetic term then becomes

$$\sigma_d = \frac{e^2}{3mc^2} \sum_j \langle \phi_j | \frac{1}{r} | \phi_j \rangle . \qquad \text{(II-36)}$$

In the LCAO approximation, each molecular orbital ϕ_j is written as a linear combination of orthonormal, hydrogenic atomic orbitals:

$$\phi_j = \sum C_{ij} \lambda_i . \qquad \text{(II-37)}$$

Substitution of (II-37) into (II-36) gives

$$\sigma_d = \frac{e^2}{3mc^2} \sum_j \langle \sum_i C_{ij} \lambda_i | \frac{1}{r} | \sum C_{ij} \chi_i \rangle$$

$$= \frac{e^2}{3mc^2} \sum_j \sum_{i,k} (2 C_{ij}^* C_{kj}) \langle \lambda_i | \frac{1}{r} | \lambda_k \rangle \qquad \text{(II-38)}$$

$$= \frac{e^2}{3mc^2} \sum_{i,k} P_{ik} \langle \lambda_i | \frac{1}{r} | \lambda_n \rangle$$

where P_{ik} is an element of the charge-bond order matrix. If we restrict our set of basis functions to just s and p orbitals on the nucleus of interest, then the only non-vanishing terms above are those of the form $\int \lambda_{1s}^{*} r^{-1} \lambda_{1s}$, $\int \lambda_{2s}^{*} r^{-1} \lambda_{2s}$ and $\int \lambda_{2p}^{*} r^{-1} \lambda_{2p}$. If these integrals are used to define an average value of $\frac{1}{r}$, then one has finally,

$$\sigma_d = \frac{e^2}{3mc^2} \sum_{\mu}^{N} P_{\mu\mu} \langle \frac{1}{r} \rangle_{\mu\mu} \qquad \text{(II-39)}$$

where μ is summed over 1s, 2s, 2px, 2py, and 2pz.

The paramagnetic term is more tedious to deal with. The zz-component of the paramagnetic tensor may be written as

$$\sigma_p^{zz} = -4 \mathrm{Re} \sum_n \frac{\langle \psi_n | \sum_k \frac{\hat{M}_{zk}}{r^3} | \psi_o \rangle \langle \psi_o | \sum_k \hat{M}_{zk} | \psi_n \rangle}{E_n - E_o}$$

$$\hat{M}_{zk} = \frac{ie\hbar}{2mc} \left[x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right]_k \qquad \text{(II-40)}$$

$$\equiv \left[\frac{ie\hbar}{2mc} \frac{\partial}{\partial \phi} \right]_k .$$

Again, making use of Slater's rules for evaluating the matrix elements, equation (II-40) may be cast in the form

$$\sigma_p^{zz} = -4 \mathrm{Re} \sum_{j,j'} \frac{\langle \phi_{j'} | \hat{M}_z / r^3 | \phi_j \rangle \langle \phi_j | \hat{M}_z | \phi_{j'} \rangle}{\epsilon_{j'} - \epsilon_j}$$

$$= -8\,\mathrm{Re} \sum_{i,k} \sum_{\ell,m} \sum_{j,j'} \frac{C_{ij}^{*}\, C_{kj'}\, C_{\ell j'}^{*}\, C_{mj}}{\epsilon_{j'} - \epsilon_{j}} \times \langle \lambda_i | \frac{\hat{M}_z}{r^3} | \lambda_k \rangle \times \langle \lambda_\ell | \hat{M}_z | \lambda_m \rangle \qquad \text{(II-41)}$$

Molecular orbitals that are unoccupied are denoted by a primed index.

Final simplification can be achieved once we know how $\hat{M}_z$ operates on the atomic orbitals. Since any component of $\hat{M}$ is a function of angle (either θ or ϕ), then it is clear that s-atomic orbitals can make no contribution in equation (II-41). The following table of matrix elements is easily verified. The first integral in equation (II-41) can be approximated by removing the r^{-3} factor and defining an

Table 4. Angular Momentum Matrix Elements for $\hat{M}_z$

	$2p_x$	$2p_y$	$2p_z$
$2p_x$	0	$\frac{ie\hbar}{2mc}$	0
$2p_y$	$-\frac{ie\hbar}{2mc}$	0	0
$2p_z$	0	0	0

average value. Since this factor drops off very rapidly, we restrict λ_i and λ_k to only atomic orbitals centered on the magnetic nucleus. The indices ℓ and m can run over all atoms, but in any pair (ℓ, m) we restrict both λ_ℓ and λ_m to be confined to the same atom, <u>i.e.</u>,

only one-center integrals are retained. The final expression becomes

$$\sigma_p^{zz} = -8\beta^2\langle r^{-3}\rangle_{2p} \sum_B \sum_j \sum_{j'} \frac{(C_{jxN}C_{j'yN} - C_{j'xN}C_{jyN})}{\epsilon_{j'} - \epsilon_j} \times (C_{jxB}C_{j'yB} - C_{j'xB}C_{jyB}) \qquad \text{(II-42)}$$

where $\beta = e\hbar/2mc$, $\langle r^{-3}\rangle_{2p}$ is an average value of the operator for 2p electrons, B runs over all atoms (except hydrogens) including the nucleus of interest (N), j runs over occupied molecular orbitals, and j′ runs over all unoccupied molecular orbitals. Similar expressions may be deduced for the xx- and yy-components of the tensor.

The Pople theory of nuclear shielding found immediate application to the vexatious problem of the unusually high shielding parameter (ca. 252 ppm upfield from HF) of chlorine monofluoride (41, 42). The average-energy approximation was shown to be untenable for ClF. It is interesting to note that of the other known fluorides of chlorine, the trifluoride resonances come about 300 ppm downfield from HF, while the pentafluoride shows resonances at 460 and 620 ppm below HF.

A product of the Pople formalism is the quantitative demonstration that carbon-13 chemical shifts are dominated by the paramagnetic term. Although Pople did not report any fluorine-19 chemical-shift calculations, one is led to believe that the same statement should apply to this nucleus. This belief is brought home forcefully by making a plot of experimental carbon-13 chemical shifts versus

experimental fluorine-19 shifts. Data for the plot in Figure 3 are tabulated in Table 5. The near linearity of the plot suggests that carbon and fluorine shielding operate by similar mechanisms.

Table 5. Carbon-13 and Fluorine-19 Chemical Shifts for Structurally Analogous Compounds

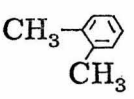
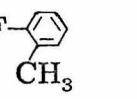
Carbon Compound	δ(C-13) (ppm)	δ(F-19) (ppm)	Fluorine Compound	Reference
CH_3–F	0	0	F–F	a
CH_3–OCH_3	16	165	F–OF	a
*CH_3–O(C=O)CH_3	23	230	*F–O(C=O)F	b, e
CH_3–$N(CH_3)_2$	28	290	F–NF_2	a
CH_3–CCl_3	29	430	F–CCl_3	a, d
*CH_3–$CCl(CH_3)_2$	41	460	F–$CClF_2$	a, d
CH_3–$C(CH_3)_3$	44	492	F–CH_3	a, d
CH_3–CHO	46	388	F–CHO	a
CH_3–$COCH_3$	51	380	F–$COCH_3$	a
CH_3–C_6H_5	53	543	F–C_6H_5	a
*CH_3–CO_2CH_3	54	476	*F–CO_2F	b, e
	55	548		a
CH_3–CH_2F	61	575	F–CH_2F	a
CH_3–CH_3	70	704	F–CH_3	a
CH_3–CN	71	589	F–CN	a

Table 5 (Cont'd)

Carbon Compound	δ(C-13) (ppm)	δ(F-19) (ppm)	Fluorine Compound	Reference
CH_3–$Si(CH_3)_3$	76	592	F–SiF_3	a, c
CH_3–$Ge(CH_3)_3$	77	608	F–GeF_3	a
CH_3–H	78	627	F–H	a

[a] Data are taken for the most part from appropriate tables in J. W. Emsley, J. Feeney and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1966, Vol. 2.

[b] Carbon data from unpublished work of Dr. Manfred Jautelat.

[c] Note incorrect fluorine datum in Table 11.5 of reference a.

[d] Recent measurements in these laboratories indicate that some of the data on the fluoromethanes that was reported by Gutowsky in 1953 may be in error by 5-15 ppm: L. H. Meyer and H. S. Gutowsky, J. Phys. Chem., 57, 481 (1953).

[e] R. L. Cauble and G. H. Cady, J. Amer. Chem. Soc., 89, 5161 (1967).

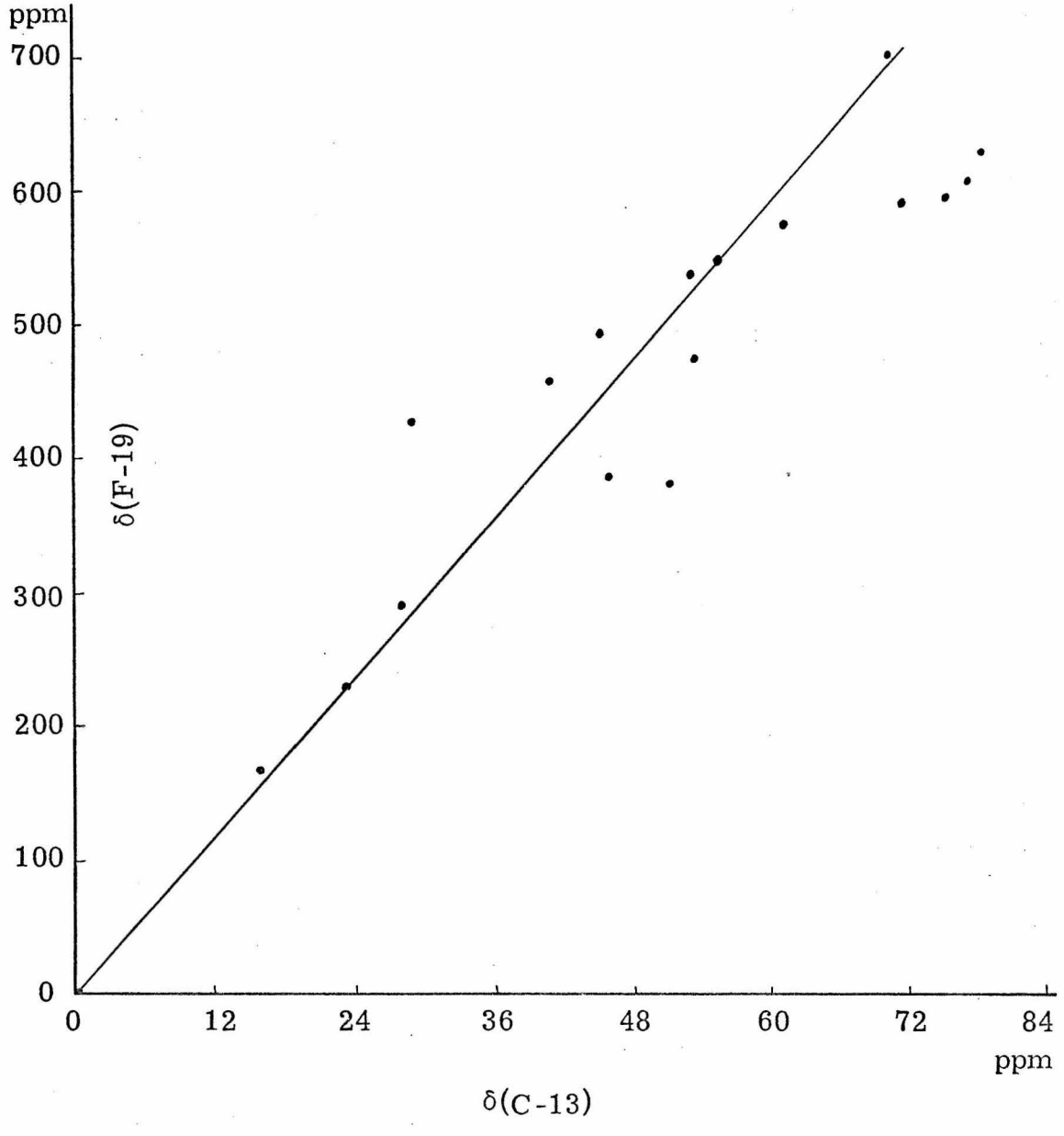


Figure 3. Plot of fluorine-19 chemical shifts vs carbon-13 chemical shifts

III. Statement of the Problem

One of the most successful applications of nuclear magnetic resonance spectroscopy to chemical problems has been to problems in conformational analysis (43). Specific applications of the fluorine nucleus are to be found in the papers by Tiers on perfluorocyclohexane (44), Bovey and co-workers on fluorocyclohexane (45), Gutowsky and Allerhand on 1,1-difluorocyclohexane (46), Reeves and Wells on perfluoropiperidine (47), Newmark and Sederholm on ethane rotamers (48), Roberts and co-workers on substituted 1,1-difluorocyclohexanes and 2,2-difluorodecalins (49), and Thomas on perfluorocyclooctane (50). For the most part, inferences about conformational phenomena have come from analysis of spectra as a function of temperature. Relatively little attention has been given to a detailed interpretation of the chemical shifts which are measured. The theory of spin-spin coupling appears to have been more easily adapted to discussion of structural features than has the theory of nuclear shielding.

Consider the plight of an investigator confronted with just the data of columns 1 and 4 in Table 6-8. How is he to make sense out of this welter of numbers?

Table 6. ^{19}F Data for Various Fluorinated Decalins

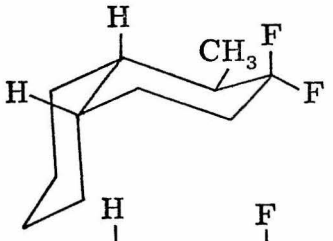
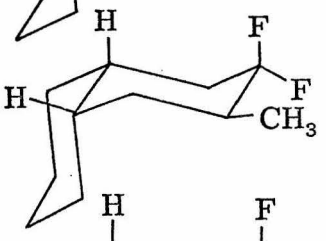
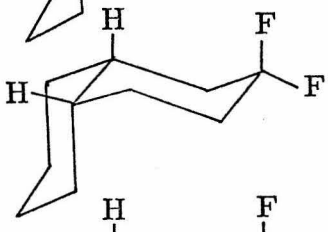
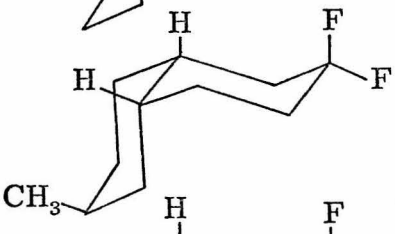
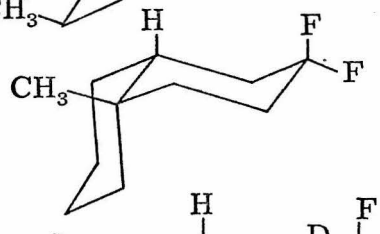
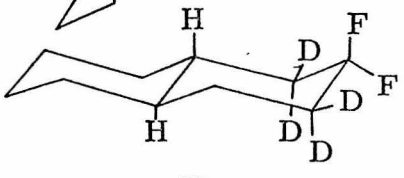
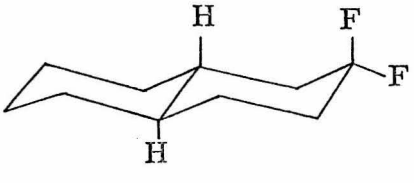
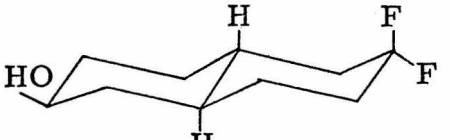
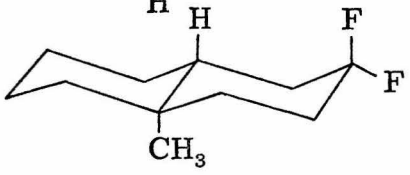
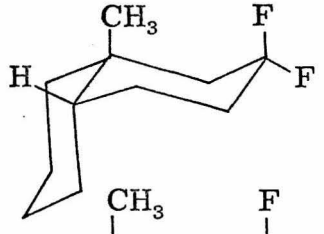
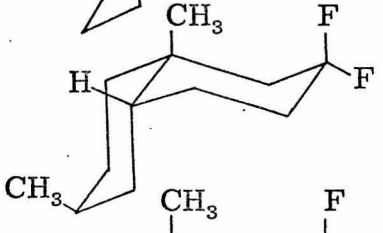
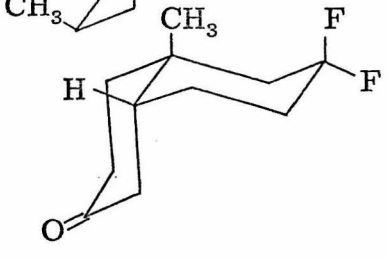
Compound[a, b]	Equatorial F	Axial F	δ_{FF}(°T)
	3747	2616	1131 (RT)
	3626	2186	1040 (RT)
	4246	3485	761 (-80)
	4240	3481	759 (RT)
	4141	3428	713 (-80)
	4119	3413	696 (RT)
	4155	3498	657 (RT)

Table 6. (Cont'd)

Compound	Equatorial F	Axial F	δ_{FF}(°T)
	4140 [c]	3500 [c]	640 [c] (RT)
	4188	3551	587 (RT)
	4388	3844	544 (-80)
	4542	4135	407 (RT)
	4469 [d]	4145 [d]	324 [d] (-80)

[a] All data taken from J. T. Gerig and J. D. Roberts, J. Amer. Chem. Soc., 88, 2791 (1966) unless otherwise indicated.

[b] Data taken at 56.4 MHz and are in Hz downfield from C_6F_6 according to the approximate relation $\delta(C_6F_6) = \delta(CF_3COOH) - 4839$ Hz.

[c] Approximate values taken from the paper by Dewar: M. J. S. Dewar and T. G. Squires, J. Amer. Chem. Soc., 90, 210 (1968).

[d] Unpublished data of Dr. Ruth E. Lack.

Table 7. ^{19}F Data for Various Fluorinated Cyclohexanes

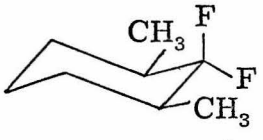
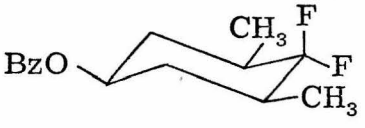
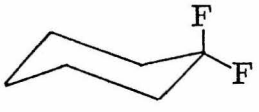
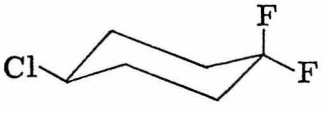
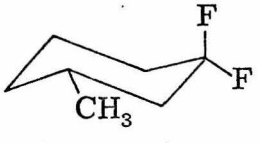
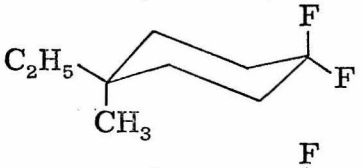
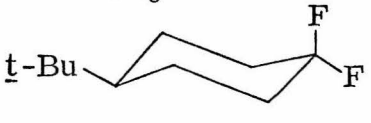
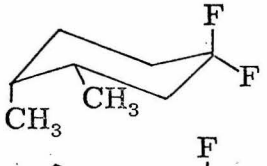
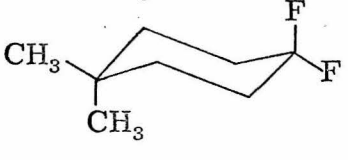
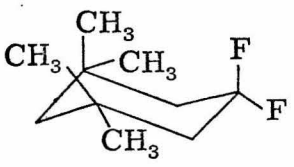
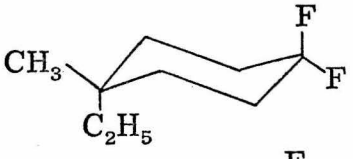
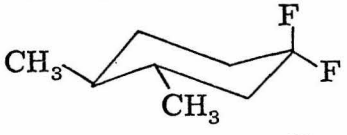
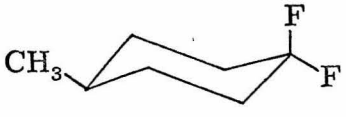
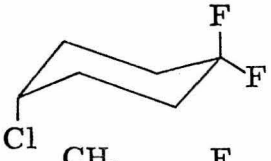
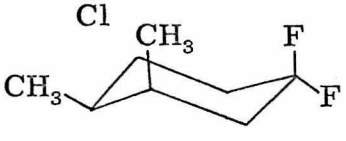
Compound[a, b]	Equatorial F	Axial F	δ_{FF}(°T)
	3177[c]	1639[c]	1538[c] (RT)
	2832[d]	1594[d]	1238[d] (RT)
	4201	3317	884 (<-46)
	4072[e]	3276[e]	796[e] (-75)
	4130	3416	714 (RT)
	4036[e]	3330[e]	706[e] (-75)
	3985	3313	672 (RT)
	4212[f]	3546[f]	666[f] (RT)
	3997	3343	654 (-80)

Table 7. (Cont'd)

Compound	Equatorial F	Axial F	δ_{FF}(°T)
	4667 [c]	4024 [c]	643 [c] (<-50)
	4028 [e]	3386 [e]	642 [e] (-75)
	4109 [f]	3479 [f]	630 [f] (RT)
	3940	3330	610 (RT)
	3814 [e]	3320 [e]	494 [e] (-75)
	4326 [f]	3931 [f]	395 [f] (RT)

[a] All data taken from S. L. Spassov, D. L. Griffith, E. S. Glazer, K. Nagarajan and J. D. Roberts, J. Amer. Chem. Soc., 89, 88 (1967) unless other wise indicated.

[b] Data taken at 56.4 MHz and are in Hz downfield from C_6F_6 according to the approximate relation $\delta(C_6F_6) = \delta(CF_3COOH) - 4839$ Hz.

[c] Unpublished data of Dr. Klaus Grohmann.

[d] Unpublished data of Dr. Robert D. Stolow.

[e] Conformation is not certain.

[f] Unpublished data of Dr. Ruth E. Lack.

Table 8. ^{19}F Data for Miscellaneous Fluorides[a]

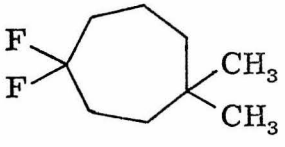
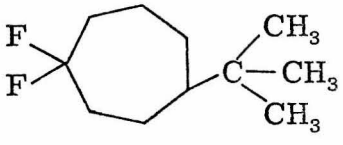
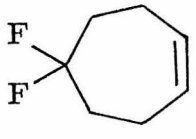
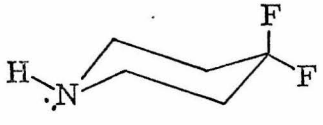
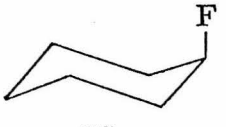
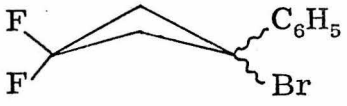
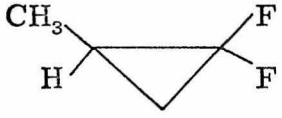
Compound	Upfield F	Downfield F	δ_{FF}(°T)
			841[b] (-150)
			185[b] (RT)
	4691	6293	1602[c] (-115)
			970[d] (-87)
	-1341		
vs.			1156[e] (-88)
		-185	

Table 8. (Cont'd)

Compound	Upfield F	Downfield F	δ_{FF}(°T)
			1175[f] (-87) 40
			1210[f] (-87) 960
			948[g] (RT)

[a] Data reported at 56.4 MHz and are in Hz downfield from C_6F_6 according to the approximate relation $\delta(C_6F_6) = \delta(CF_3COOH) - 4839$ Hz.

[b] E. S. Glazer, Ph.D. Thesis, California Institute of Technology, 1966.

[c] R. Knorr, C. Ganter and J. D. Roberts, Angew. Chem., 79, 577 (1967).

[d] Unpublished data of Dr. Ghariballa Yousif.

[e] F. A. Bovey, E. W. Anderson, F. P. Hood and R. L. Kornegay, J. Chem. Phys., 40, 3099 (1964).

[f] J. B. Lambert and J. D. Roberts, J. Amer. Chem. Soc., 87, 3884 (1965).

[g] W. D. Phillips, J. Chem. Phys., 25, 949 (1956).

In order to properly dissect the data, it is best to consider compounds within a given related class, e.g., the class of trans-2,2-difluorodecalins, rather than attempt a broad overall inspection. Further, it soon becomes apparent that trends are more easily discerned if one examines not the fluorine-fluorine chemical-shift differences but rather the individual shieldings of the two fluorines.

There is not yet available enough data for four-membered ring systems, seven- and eight-membered ring systems, and six-membered ring systems containing heteroatoms to permit a detailed analysis; the discussion here will therefore be limited to the cyclohexane and decalin systems. The following trends emerge from the data:

(1) In both series of compounds, variations in the shielding of the equatorial fluorines are more pronounced than those of the axial fluorines.

(2) Substituents in the 4-position of 1,1-difluorocyclohexane shift the equatorial fluorine to higher field, and this shift appears to be greater when the substituent is axial. The eighth and twelfth entries in Table 7 are structurally analogous to 2,2-difluoro-cis- and trans-decalin, respectively; we would therefore predict the equatorial fluorine of the former to resonate at lower field than that of the latter.

(3) Substituents at the γ-carbon* of either system generally move one or both fluorine resonances downfield, regardless of whether the substituent occupies an axial or an equatorial position.

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* For example, C-3 in 1,1-difluorocyclohexane.

Effects are larger when the substituent is axial, and in this case the axial fluorine resonance is the more strongly affected.

(4) Substituents at the β-carbon of either 1,1-difluorocyclohexane or 2,2-difluorodecalin strongly shift both fluorine resonances to higher field, generally by 15-20 ppm.

It should be pointed out that the word "substituent" has been used more generally than the data allow, since in most cases only the effects produced by methyl groups have been investigated. Strongly electron-withdrawing groups such as $-C\equiv N$ or $-COOH$ might cause reversals or other striking changes in the trends.

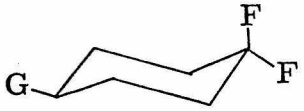
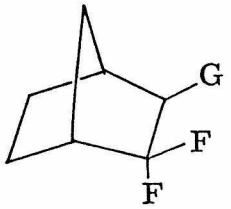
For purposes of discussion it is convenient to designate those effects arising from substitution at the β-carbon, i.e., the 1- or 3-positions of 2,2-difluorodecalin, as proximate effects. Effects due to substituents more remotely placed will then be called long-range effects. This division is also convenient for another reason: our intuition tells us that it may be easier to sort out the factors or the major factor responsible for the proximate effects than for the long-range effects. Certainly our intuition would suggest to us that it ought to be the more sterically congested, axial fluorine which receives the brunt of the effect of a change of substituent. Further, our intuition might suggest that substitutions at the γ- and δ-carbons are basically similar processes and both should thus result in either an upfield shift or a downfield shift of the fluorine resonances, although a priori it might be difficult to know which case to expect. The data of Tables 6 and 7 clearly show that substitution at the

γ-carbon is unique in some manner.

A substituent at the 3-position and a substituent at the 4-position possess different geometrical relationships to a given fluorine in the cyclohexane system. This fact prompts one to explore the utility of the simple distance-angle formula that was derived by McConnell (equation II-33). The McConnell formula, somewhat modified by ApSimon who removed the restriction that the magnetic dipole be considered a point dipole (51), was applied to two systems. In these calculations one first estimates the contribution to the shielding of a particular nucleus by a remote hydrogen (σ_N^H); the calculations are then repeated on the same system with the hydrogen replaced by a methyl group ($\sigma_N^{CH_3}$). Subtraction then gives the chemical shift between the two compounds. Table 9 presents the results of these calculations; coordinates needed for the cyclohexanes were obtained by use of a coordinate program written by P. M. Kuznesof, and coordinates for the norbornanes were obtained through the vector model of C. F. Wilcox (52).

The results show clearly that the McConnell treatment is inadequate, at least for the present two systems. Grant and Cheney have pointed out that because anisotropic terms describe field effects which are a property of the perturbing group and not of the nucleus under consideration, protons and heavier nuclei should be affected alike when they are positioned in an equivalent spatial configuration (53). Since shifts of the order of 15-20 ppm are not observed for protons, anisotropy cannot account for more than a few percent of the

Table 9. Anisotropy Calculations on Two gem-Difluoride Systems

Compound	σ_F^H(ppm)	$\sigma_F^{CH_3}$(ppm)	δ(calc.)	δ(expt.)	
	0.003	0.165	0.16	-0.2	axial
	0.058	0.154	0.10	4.6	equat.
	0.31	0.682	0.37	18.6[a]	exo
	-0.195	0.01	0.21	0.3[a]	endo

[a] Results obtained from the present work.

magnitude of the shift in the case of fluorine nuclei. The statement made by Eliel (54) that "At the moment, it is an open question whether the large change caused by the distant alkyl group in the fluorine chemical shift is due to a long-range anisotropy effect of the alkyl group itself or whether it is the result of a subtle deformation of the cyclohexane framework." is probably without foundation.

Some workers have attempted to account for fluorine chemical shifts in certain cases in terms of electric fields at the fluorine which are produced by neighboring groups. Following a model devised by Pople (116) for the effect of an external electric field on the shielding

of an isolated hydrogen atom, Feeney has suggested that fluorine chemical shifts in saturated systems can be accounted for by an equation of the form

$$\delta(F) = -A\Delta E_z - B(\Delta E^2 + \Delta \langle E^2 \rangle) \qquad \text{(III-43)}$$

where E is the electric field produced at the fluorine nucleus by point dipoles placed at the center of any polar bonds in the molecule, E_z is the component of this field along the bond axis, and $\langle E^2 \rangle$ is the time-averaged square of the electric fields produced at the fluorine nucleus by fluctuating dipoles in the bonds (55). Generally, the first two terms are small compared with the third. To estimate this third term we note that the mean-square fluctuating electric field at a point distance r from an atom in its ground state is (56)

$$\langle E^2 \rangle = 2 r^{-6} \langle O | \mu^2 | O \rangle \qquad \text{(III-44)}$$

where μ is the induced dipole moment. The static polarizability P of the system is given by second-order perturbation theory as

$$P_{xx} = 2 \sum_n{}' \frac{\langle O | \mu_x | n \rangle \langle n | \mu_x | O \rangle}{E_n - E_o} \qquad \text{(III-45)}$$

for the xx-component of the tensor (57). By defining an average energy and using quantum mechanical closure one can simplify equation (III-45) to

$$P = \frac{2}{3\Delta E} \langle O | \mu^2 | O \rangle \qquad \text{(III-46)}$$

where ΔE is to be identified approximately with a group ionization potential I. Hence, we have finally,

$$\langle E^2 \rangle = 2 r^{-6} \left(\frac{3 PI}{2}\right) = 3 \sum_i P_i I_i / r_i^6 \qquad \text{(III-47)}$$

where i runs over all polar substituents under consideration. The simplified Feeney expression is therefore

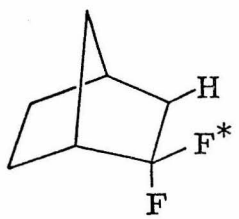
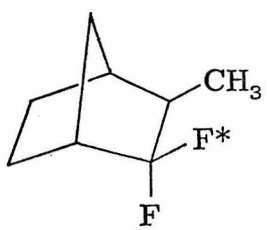
$$\delta(F) = -3 B \Delta \sum_i P_i I_i / r_i^6 \qquad \text{(III-48)}$$

The constant B applies to a given type of system, i.e., cyclohexane system, ethane rotamer, cyclobutane system, etc.

The result of applying equation (III-48) to a particular example is given in the table below. The predicted result is that substitution of an exo-3-hydrogen by a methyl group should shift the exo-fluorine downfield by 0.82 ppm! The experimental result, which was cited in Table 9, is an upfield shift of 18.6 ppm. Once again, it becomes clear that a naïve treatment is wholly inadequate for accounting even qualitatively for fluorine chemical shifts.

There is an additional serious stumbling block to a qualitative understanding of the data in Tables 6-8. Nearly all of the systems in these tables contain relatively flexible rings. It may be unsafe to assume that introduction of a substituent anywhere in the ring of 1,1-difluorocyclohexane will not cause a significant alteration of bond

Table 10. Electric Field Calculation on a gem-Difluoride

Compound	P (Å)	I (erg × 10^{12})	r (Å)	$-B\langle E^2 \rangle$ (ppm)
	0.667 [a]	21.8	2.302	-7.62 [c]
	2.424 [a]	7.35 [b]	2.341	-8.44 [c]

[a] Polarizabilities from K. G. Denbigh, Trans. Faraday Soc., 36, 936 (1940).

[b] Ionization potential of methyl group taken from S. W. Benson, J. Chem. Educ., 42, 502 (1965).

[c] A value of B = 26 × 10^{-18} esu was used; see reference 55.

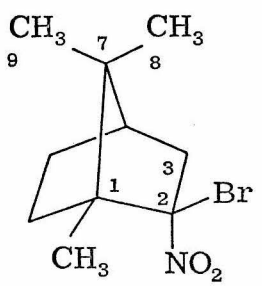
angles and interatomic distances, at least significant enough to substantially affect the shielding of either fluorine. It would be nice to have available X-ray or electron-diffraction data for several members of a series so that one could actually see what the effect of placing various substituents on a cyclohexane ring is really like. Ordinary molecular models certainly do not militate against the

possibility that six-membered rings are at least somewhat flexible. In principle, one might approach this problem through calculations of the type done by Hendrickson (58), Wiberg (59) or Allinger (60) on ground-state geometries, using the fluorine potential functions, perhaps, due to Vanderslice and co-workers (61). It is still too early to assess the reliability of this approach.

Nevertheless, if one accepts the hypothesis that conformational ambiguity can be a source of difficulty in interpreting trends in fluorine chemical-shift data, it seems reasonable that one ought to start with systems where this ambiguity is minimal. Three-membered rings are a possibility here, but these offer only two different geometries for substituent and fluorine. A better alternative is provided by the relatively rigid norbornane system. Many different geometries are possible (ca. 30) between a substituent and a fluorine atom; accordingly, the object of this research was to prepare a number of substituted 2,2-difluoronorbornanes for chemical-shift measurements. Only the methyl group was used as a substituent, so that possible correlations of shielding with geometry could be sought for, leaving for later a search for correlations with intrinsic electronic properties of the substituents.

IV. Results and Discussion

It is convenient to reiterate that the reason for having selected the norbornane skeleton as the system of choice on which to hand a suitable magnetic probe (a fluorine atom) and one or more substituents is that this skeleton is likely to be comparatively rigid, thus allowing a reasonable degree of certainty in assigning coordinates to all relevant atoms. For structure (I), for example, it would be expected

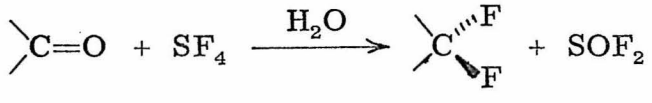


(I)

that the bromine atom would seriously interact with the syn-7-methyl group; relief from this interaction could be achieved by twisting the plane of the two methyl groups about carbon-7 as a pivot point, thus making the distance C2-C8 greater than the distance C3-C8. A crystallographic study by Robertson and students shows that there is little difference between these two distances; C2-C9 is 3.03 A° and C3-C9 is 2.98 A° (62). This argument is, of course, subject to question since the data refer to the solid state where one must take into

account interactions with neighboring molecules. In addition, no molecule is truly rigid. Even benzene rings are somewhat flexible and can be distorted, as is well known for [2.2]paracyclophanes.

Methyl substituents were placed at all positions of the 2,2-difluoronorbornane ring skeleton except the 4-position. In general, the gem-difluorides were prepared by reaction of the corresponding ketone with sulfur tetrafluoride in the presence of some acidic component, usually hydrogen fluoride generated in situ, whose function is not known with certainty (63). The proclivity of certain



norbornyl derivatives to rearrange under acidic conditions is well known; however, in none of the sulfur tetrafluoride reactions was there any rearrangement observed. This suggests that the fluorination reaction may proceed through some sort of S_Ni-type mechanism in which a significant positive charge at the carbonyl carbon never builds up.

Proof that there was in each case only one gem-difluoride present, at least in major proportions, was indicated by the fact that the fluorine nmr spectra consisted of just a single AB-type pattern. Additional analytical data obtained for each difluoride consisted of a vapor-phase chromatogram to indicate homogeneity, a microanalysis to indicate the correct empirical formula, and an infrared spectrum.

Some of the gem-difluorides proved to be solids and some were liquids. The parent material, 2,2-difluoronorbornane, is a white, crystalline solid, mp 73°. It was readily prepared in 55% yield by fluorination of norcamphor. On the other hand, introduction of a methyl group at the 3-position destroys some of the symmetry of the system and must influence strongly the packing of the molecules; exo-3-methyl-2,2-difluoronorbornane is a colorless liquid, bp 125-126°, although the endo isomer is again a crystalline solid, mp 53-54°. These two difluorides were prepared by the methods outlined in Figure 4. The difluorides derived from camphenilone (3,3-dimethylnorcamphor) and 1-methylnorcamphor also proved to be solids.

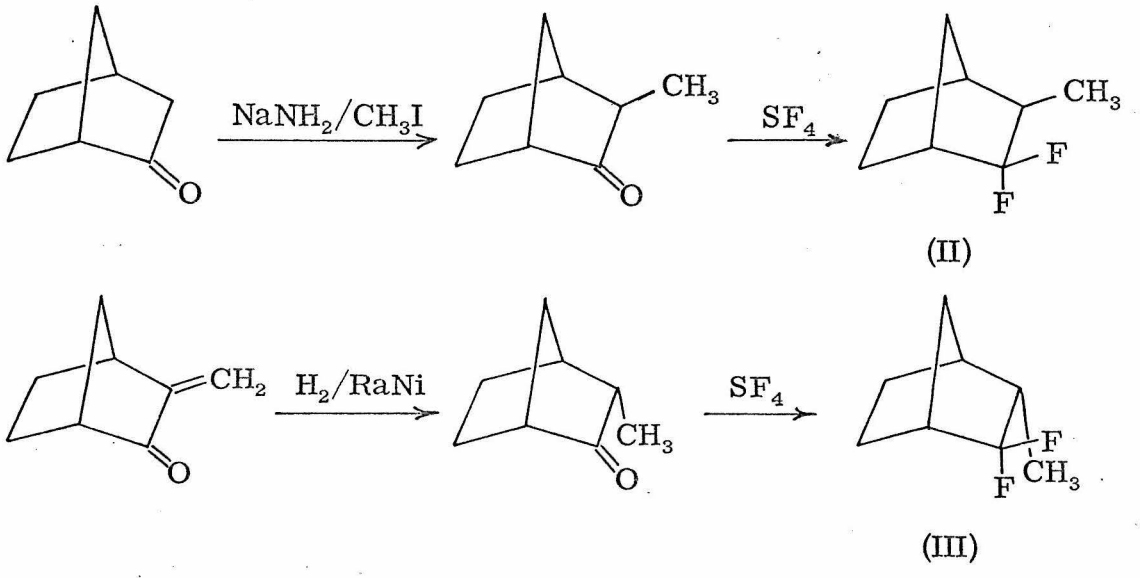
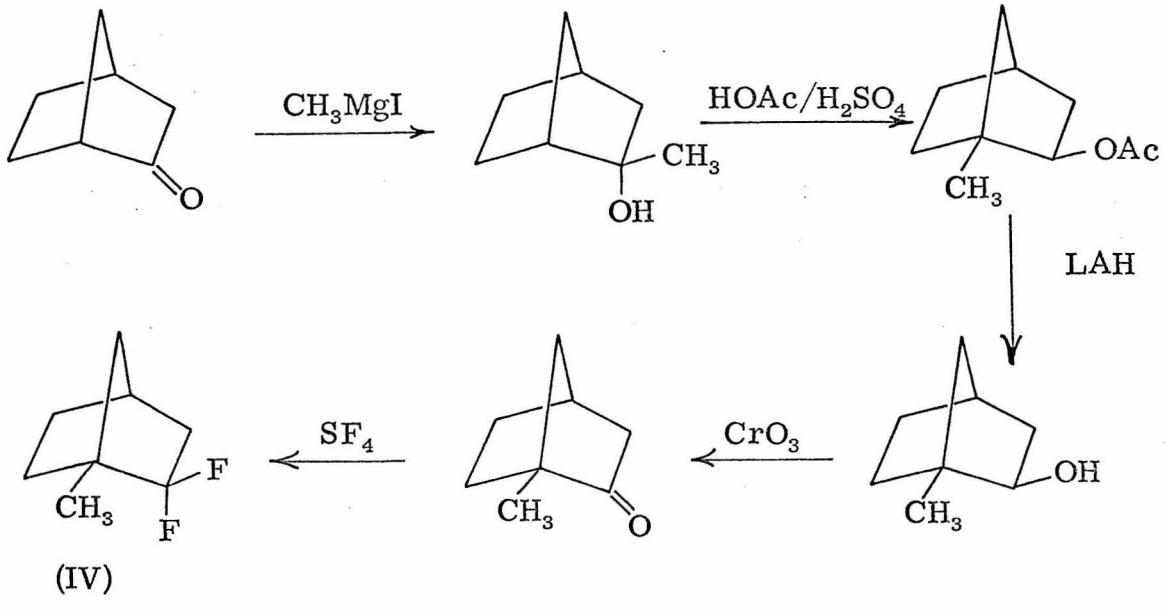


Figure 4. Synthesis of exo-3-methyl-2,2-difluoronorbornane (II) and endo-3-methyl-2,2-difluoronorbornane (III)

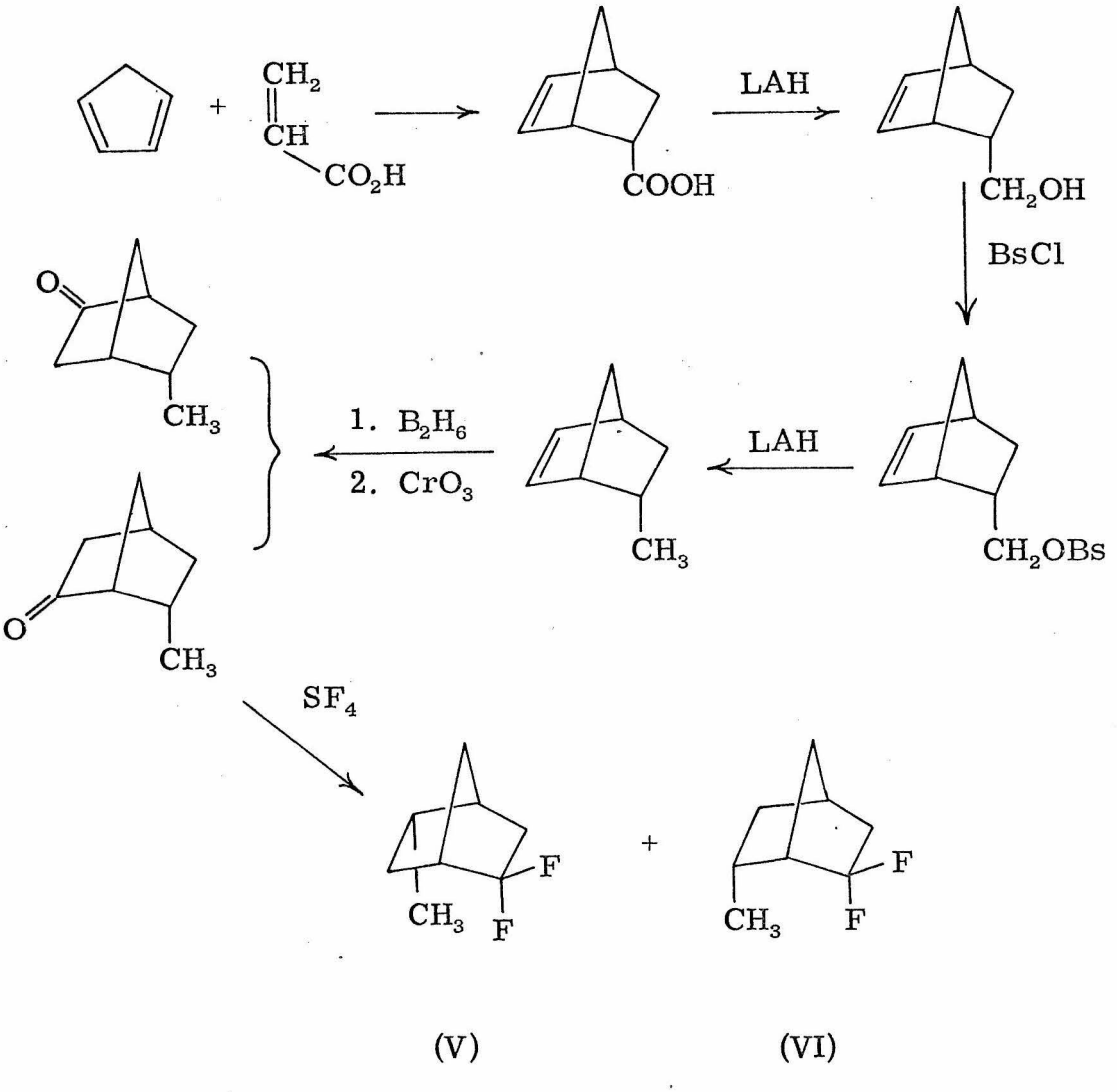
The ketonic precursor to the latter difluoride was made via a Wagner-Meerwein rearrangement as shown in the figure below.



(IV)

Figure 5. Synthesis of 1-methyl-2,2-difluoronorbornane (IV)

In devising a synthesis for norcamphor substituted with methyls at the 5-position or 6-position, it was felt that the scheme should start with an appropriate Diels-Alder reaction. For the while, it seemed more interesting to prefer to have the substituent in the endo position. The addition of allyl bromide to cyclopentadiene, followed by lithium aluminum hydride reduction to the hydrocarbon, could have been used as a reasonable route to a key intermediate (64). Instead, the route outlined in Figure 6 was followed. The endo-5-methyl-2-norbornene, which was prepared in four steps, was hydroborated and

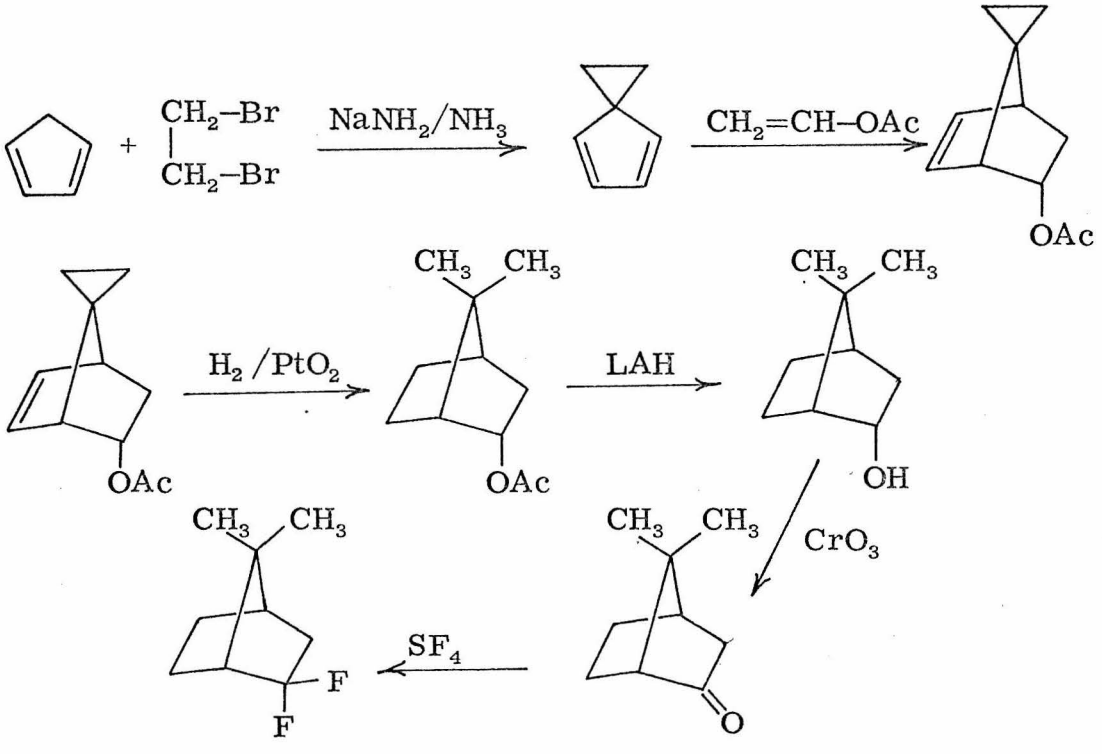


(V) (VI)

Figure 6. Synthesis of endo-5-methyl-2, 2-difluoronorbornane (V) and endo-6-methyl-2, 2-difluoronorbornane (VI)

oxidized in situ to give a nearly 1:1 mixture of both possible ketones. These were separated and identified by comparison with spectral properties of authentic samples (65). Fluorination of the ketones yielded (V) and (VI) as colorless liquids.

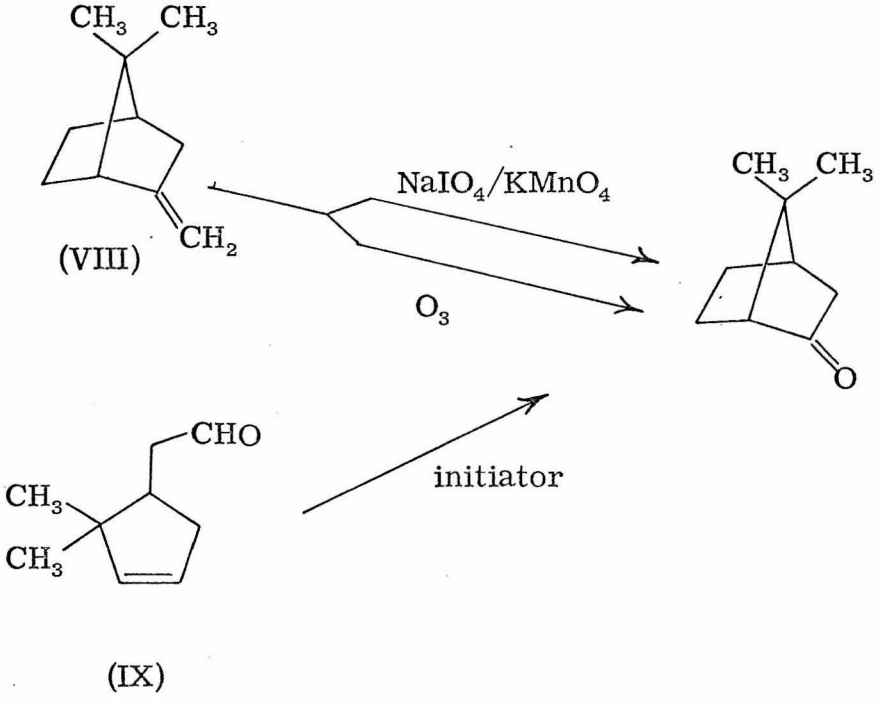
Introducing methyl groups at the 7-position of norcamphor proved to be more difficult than the previous substituions. Putting a single methyl group there, either syn or anti, is more difficult than placing a gem-dimethyl group at the 7-position. The difluoride derived from apocamphor was prepared as outlined below. Although



(VII)

Figure 7. Synthesis of 7,7-dimethyl-2,2-difluoronorbornane (VII)

the chromic acid oxidation step was actually carried out with Jones reagent, a Sarrett oxidation would probably have been preferable, so as to avoid the formation of minor amounts of rearrangement products. The gem-difluoride was obtained as a white, crystalline solid, mp 88-91°. Additional potential routes to apocamphor, which were not investigated, are the ozonization or the oxidation with periodate-permanganate (66) of α-fenchene (VIII), and the radical cyclization (67) of apocampholenic aldehyde (IX).

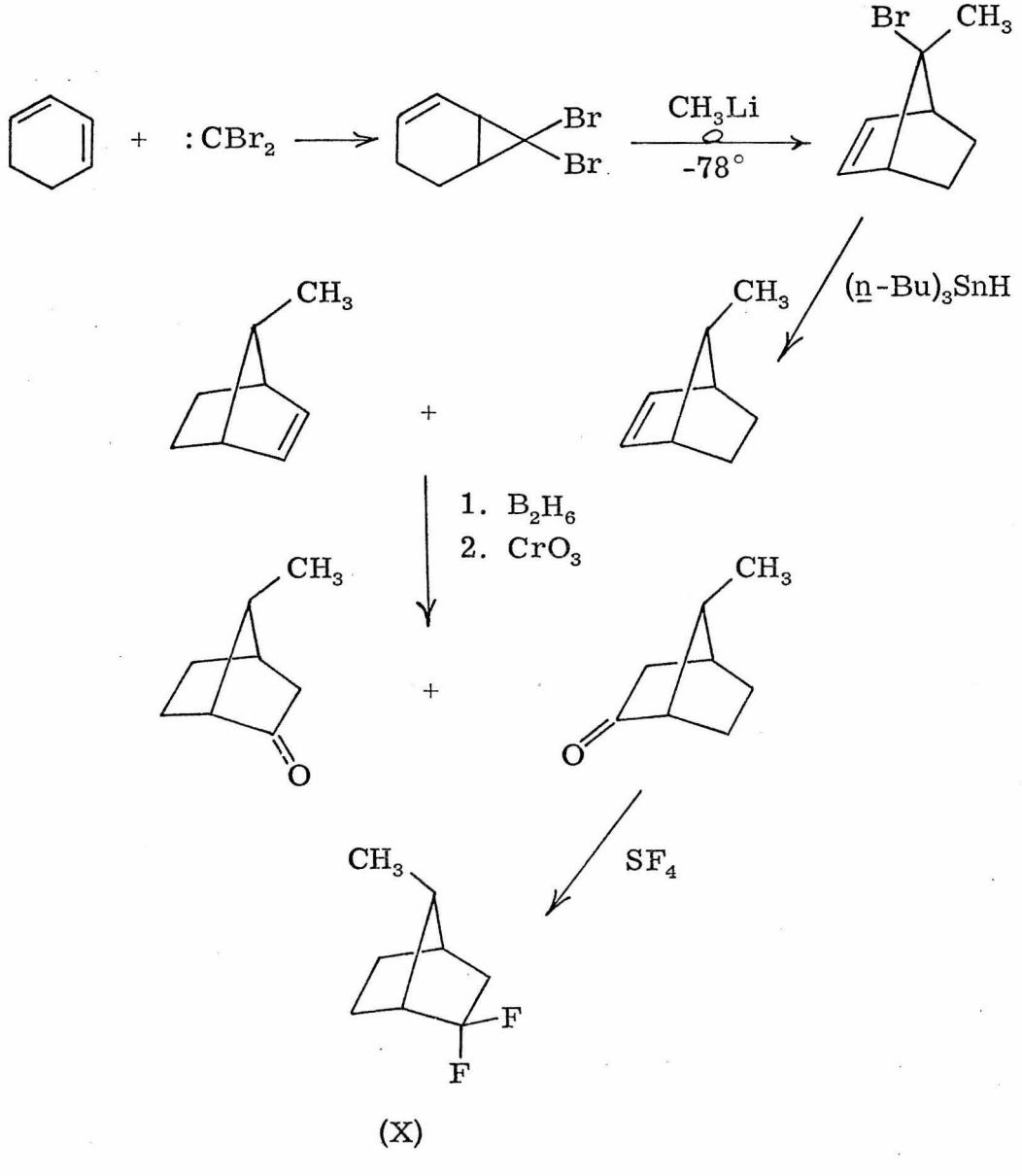


(IX)

In the first attempt to position a lone methyl group at the 7-position of norcamphor, syn-7-bromonorbornene, which is available by a nasty bromination-dehydrobromination process beginning with

norbornene (68), was treated with the recently popularized lithium dimethylcopper (69). Under the conditions recommended by Corey, the bromide appeared to be largely unreactive. At this point in the work, however, there appeared in the literature an interesting report by Skattebøl concerning the synthesis of syn-7-bromo-anti-7-methyl-norbornene (70). The opportunity which this synthesis presented was seized immediately. Figure 8 below outlines the synthetic routes which were followed in the preparation of syn- and anti-7-methyl-norcamphor. The anti-ketone was converted to the corresponding gem-difluoride (X), a colorless liquid.

Before discussing the fluorine nmr spectra of the series of 2,2-difluoronorbornanes, one point might be made concerning their infrared spectra. Bellamy states that carbon-fluorine stretching absorptions usually appear in the region 1000-1400 cm^{-1} (71). Gerig and Roberts tentatively assign bands in the 1400-1450 cm^{-1} range as being due to the carbon-fluorine stretching mode in the 2,2-difluoro-cis-decalin series (see reference a under Table 6), while Spassov et al. in their work on the difluorocyclohexanes do not cite infrared bands at positions above 1380 cm^{-1} (see reference a under Table 7). Inspection of the infrared spectra of all the compounds prepared in the present work reveals in every case a strong absorption at 1330 ± 15 cm^{-1}; there was generally an absence of any significantly intense bands in the 1380-1450 cm^{-1} region. We may therefore tentatively assign 1330 as being due to the carbon-fluorine stretching mode in the strained norbornane system. In addition, there was often a band of lesser intensity



(X)

Figure 8. Synthesis of anti-7-methyl-2, 2-difluoronorbornane (X)

occurring some 30 cm^{-1} below the 1330 cm^{-1} carbon-fluorine bond.

Fluorine nmr spectra of the difluoronorbornanes were recorded in dilute methylene chloride solutions containing a trace of hexafluorobenzene as internal standard. The spectra were calibrated with a Hewlett-Packard Audio Oscillator and are in each case the average of two spectra swept in both directions. No variable-temperature or concentration studies to investigate possible solvent effects were carried out. All spectra were recorded at 56.4 MHz with the Varian Model A-56/60A, and therefore are not proton-decoupled. Because of the broadness of the resonances, this introduces an estimated error of ±10 Hz in the reported data, but higher accuracy is not demanded by the nature of the present work. The observed pattern in every instance was a spectrum of the AB-type; this was analyzed for the fluorine-fluorine coupling constant and the chemical shifts by means of the relation

$$C = \sqrt{\delta^2 + J^2} \qquad \text{(IV-49)}$$

where C is the separation between the first and third signals of the pattern, δ is the fluorine-fluorine chemical-shift difference, and J is the fluorine-fluorine coupling constant (72).

Table 11 below summarizes the coupling constants, band widths and chemical-shift data for the nine 2,2-difluoronorbornanes that were examined. The fluorine spectrum of the parent substance, 2,2-difluoronorbornane, is of the AB-type with a fluorine-fluorine chemical-shift difference of 23.1 ppm (see Figure 9). This is a

Table 11. ^{19}F Data for 2,2-Difluoronorbornanes

Compound	Exo F[a] (bandwidth[b])	Endo F[a] (bandwidth[b])	J_{FF}[b]
H	76.1 (51)	53.0 (29)	222
1-Methyl	68.0 (49)	45.6 (28)	222
exo-3-Methyl	57.5 (22)	52.7 (27)	223
endo-3-Methyl	77.7 (46)	41.7 (12)	226
3,3-Dimethyl	62.6 (19)	43.9 (12)	224
endo-5-Methyl	76.9 (49)	50.8 (28)	221
endo-6-Methyl	87.1 (55)	59.6 (26)	228
7,7-Dimethyl	80.9 (38)	64.5 (35)	228
anti-7-Methyl	75.8 (50)	55.8 (29)	222

[a] Data in ppm downfield from C_6F_6.

[b] Data in Hz at 56.4 MHz.

larger difference than nearly every entry in Tables 6-8. The important question to be asked at this point is which fluorine corresponds to which signal. Closer examination of the spectrum reveals a great difference in the bandwidths of the A signals and the B signals (Figure 10); the upfield signals have a width at half-height of 29 Hz, whereas those downfield are 51 Hz wide. Replacement of a hydrogen at the exo-3 position by a methyl group has two important effects on the spectrum: (1) first, the downfield signals now appear some 18.6 ppm farther upfield, so that the fluorine-fluorine chemical-shift difference

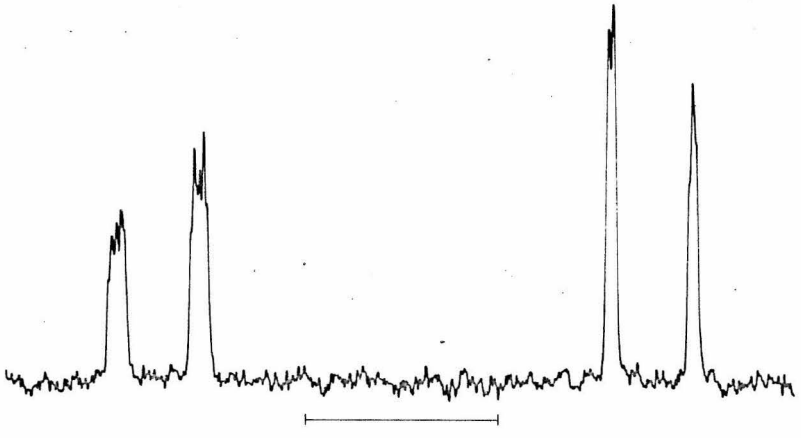


Figure 9. ^{19}F Nmr spectrum of 2, 2-difluoronorbornane

is now only 4.8 ppm (Figure 11); (2) second, the bandwidths of the downfield signals have now been drastically reduced to a mere 22 Hz. Our surmise that the downfield signals correspond to the exo-fluorine is strengthened when one now replaces, instead, the hydrogen at the endo-3 position by a methyl group. This time the upfield signals appear ca. 11 ppm farther upfield, thus resulting in a spectrum with a very large fluorine-fluorine chemical-shift difference, ca. 36 ppm (Figure 12); further, the bandwidths of these signals have now been reduced from 29 Hz to 12 Hz.

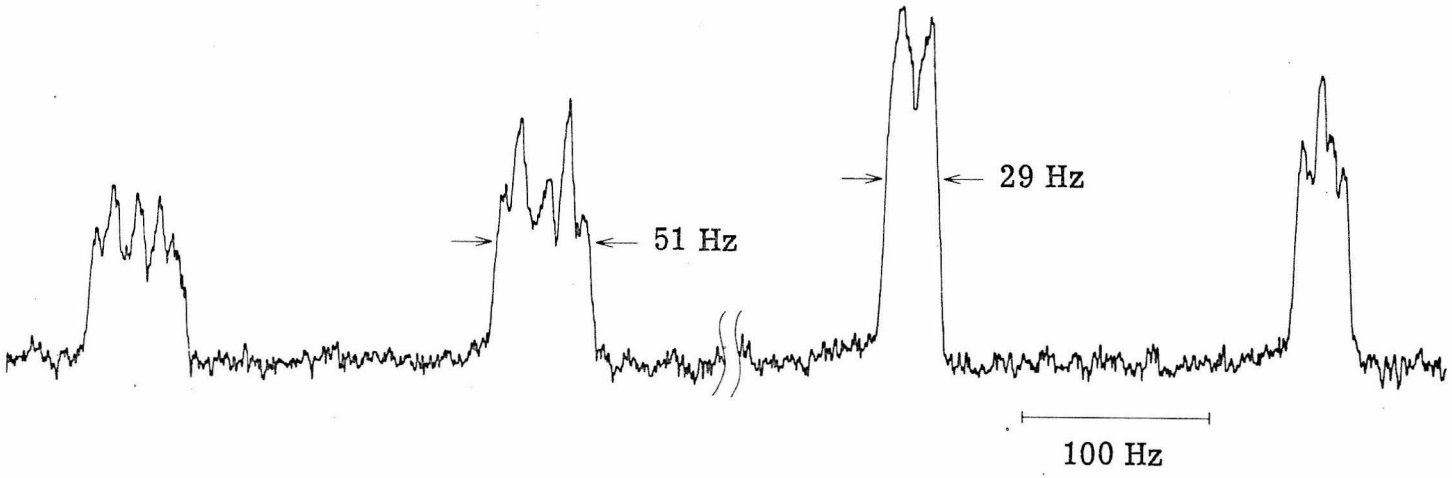


Figure 10. ^{19}F Nmr spectrum of 2, 2-difluoronorbornane

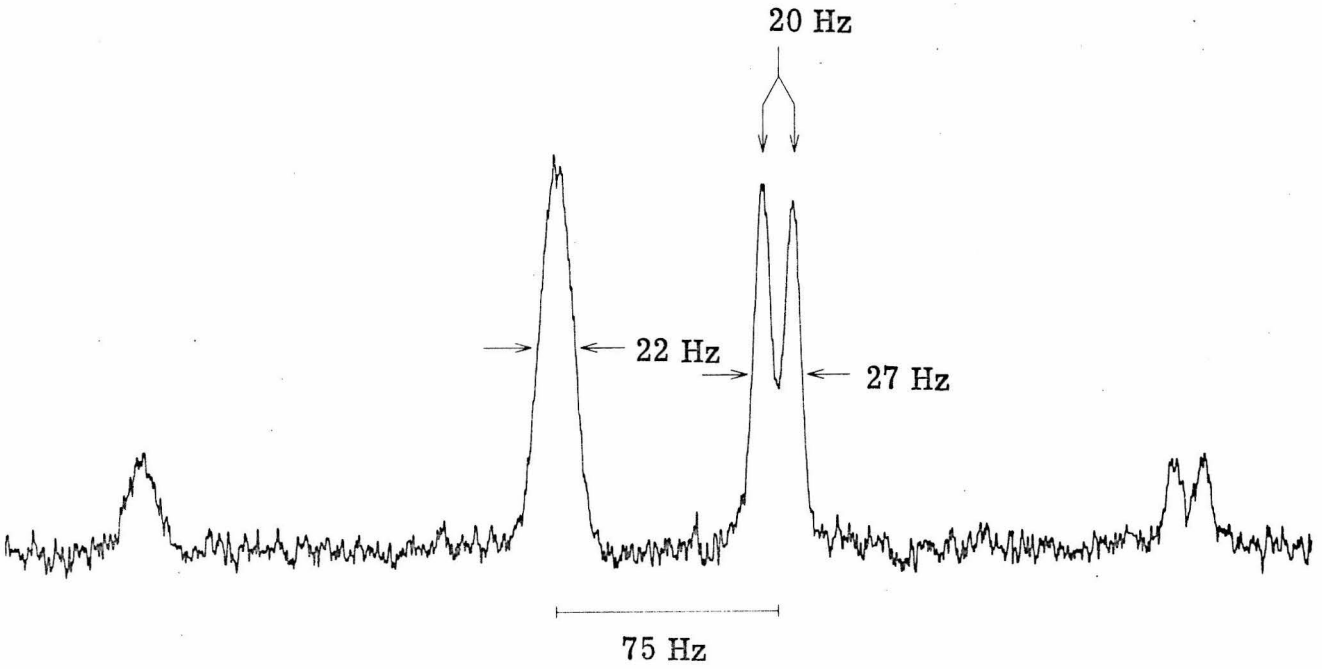


Figure 11. ^{19}F Nmr spectrum of exo-3-methyl-2,2-difluoronorbornane

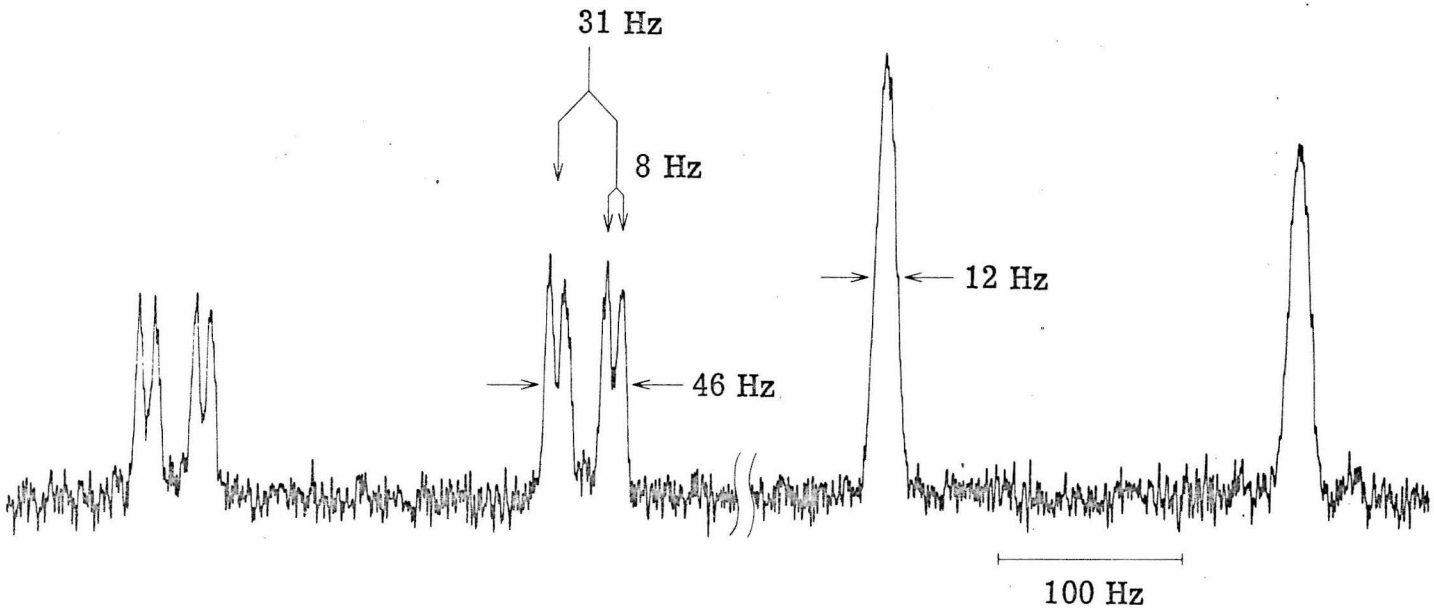
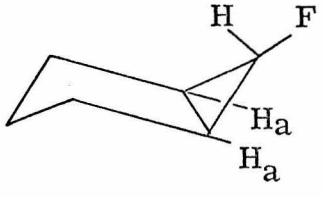
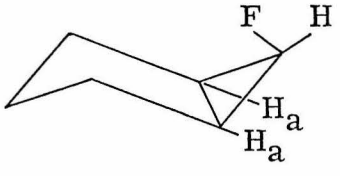


Figure 12. ^{19}F Nmr spectrum of endo-3-methyl-2,2-difluoronorbornane

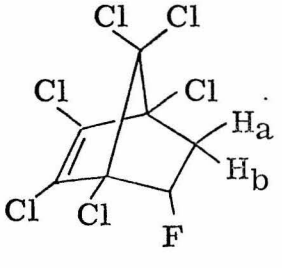
These phenomena furnish the clue to the assignment of signals. Work by several groups of investigators strongly supports the thesis that a Karplus-type curve (73) provides an adequate description of H-F coupling. Jonáš, Allerhand and Gutowsky find that at low temperature the axial-axial vicinal H-F coupling in 1,1-difluorocyclohexane is 34.3 Hz, whereas the equatorial-axial coupling is only 11.5 Hz (46). For structure (XI) the coupling constant J_{H_aF} is 21 Hz, but for (XII) it is only 10 Hz (74). The recent findings of Williamson and co-workers on H-F coupling in (XIII)-(XV) bring home the point still more



(XI)



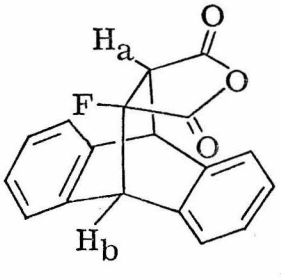
(XII)



(XIII)

$J_{H_bF} = 24.7$

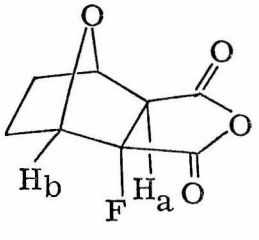
$J_{H_aF} = 12.2$



(XIV)

$J_{H_aF} = 22.5$

$J_{H_bF} = 6$



(XV)

$J_{H_aF} = 10.6$

$J_{H_bF} = 2.3$

forcefully (75). Finally, the analogous H–H couplings are known to be consistent with a Karplus-type curve in the norbornyl system (76, 77). It is not difficult to conclude, therefore, that with the 2, 2-difluoro-norbornanes it is the exo-fluorine which occurs downfield, and that substitution of a vicinal hydrogen by a methyl group eradicates some 15-20 Hz worth of cis H–F coupling in the system.

We note also that substitution by a vicinal methyl group has the effect of shifting the cis fluorine about 10-20 ppm upfield and of leaving the gauche fluorine essentially untouched. Our predictions as to the appearance of the spectra for 1-methyl-2, 2-difluoronorbornane and 3, 3-dimethyl-2, 2-difluoronorbornane relative to the parent substance would confidently run as follows:

1-Methyl -- Both fluorine resonances should be moved upfield, but not by as great an amount as in the 3-substituted cases; there should be only slight reduction in band widths of both fluorine signals.

3, 3-Dimethyl -- Both fluorine resonances should be shifted upfield by about 10-20 ppm, and both sets of signals should be relatively narrow. The spectra of these two compounds are displayed in Figures 13 and 14, and the data of Table 11 reveal that all of the predictions above are indeed correct.

Before extending the discussion to the particulars of substitution at points more remote on the norbornane ring skeleton, it is relevant to digress here and expound on another matter. According to terminology laid down earlier, we are dealing in the case of substitution by a vicinal methyl group with a proximate effect. The *effect observed* in

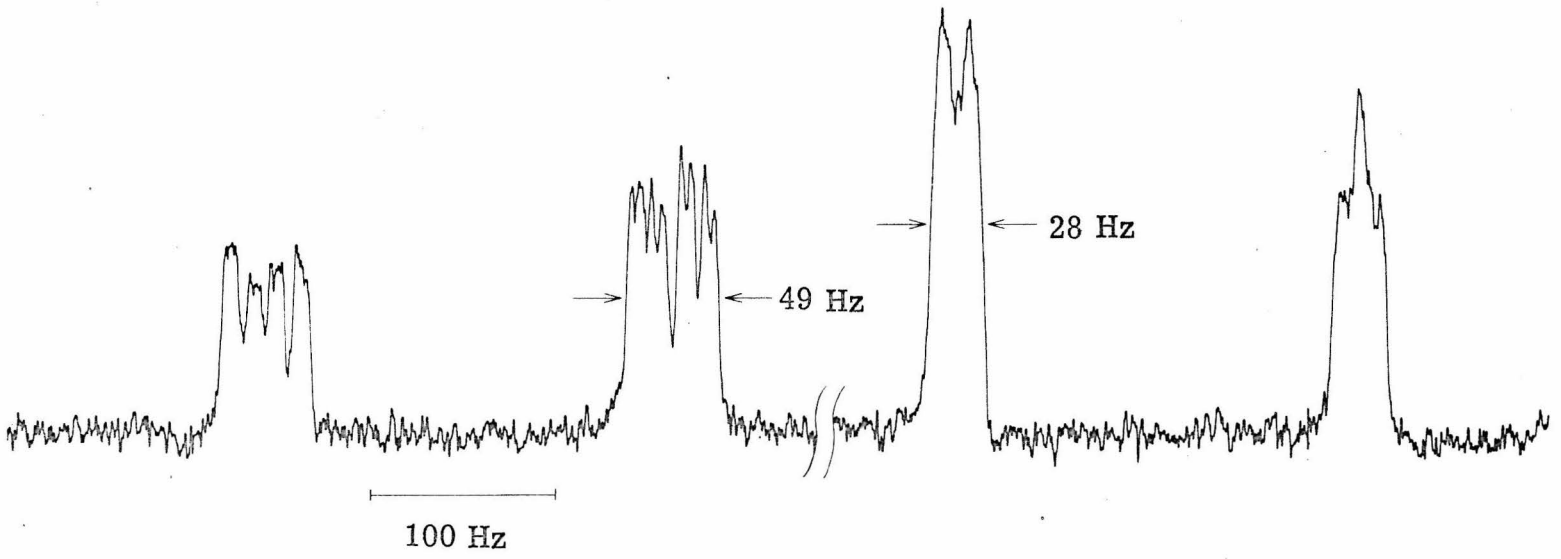


Figure 14. ^{19}F Nmr spectrum of 1-methyl-2, 2-difluoronorbornane

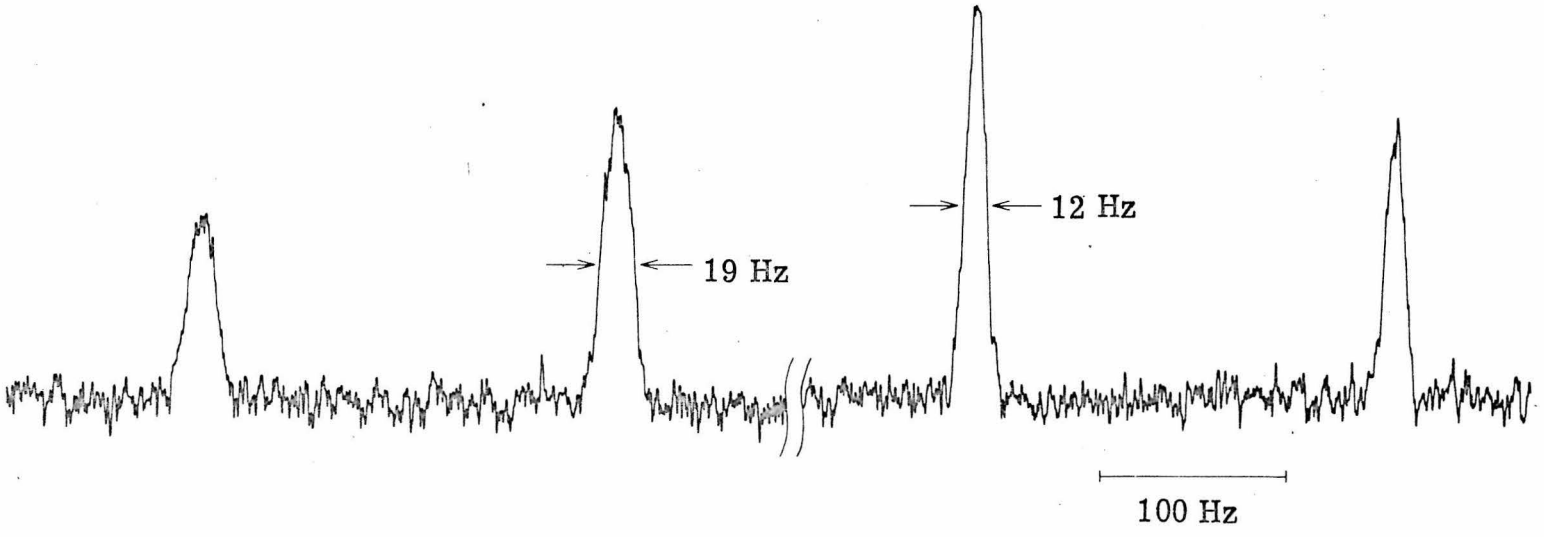


Figure 13. ^{19}F Nmr spectrum of 3,3-dimethyl-2,2-difluoronorbornane

the cyclohexane, decalin and norbornane systems is a shift to higher field of some 10-20 ppm. Similar but smaller effects are to be found in carbon-13 spectra. The chemical shift of a methyl carbon in o-xylene is about 1.8 ppm greater than that of toluene, and for the central methyl group in hemimellitene it is 6.3 ppm greater than that of toluene (78). Likewise, in the methylcyclohexane series Grant finds that introduction of a vicinal, gauche methyl group into a methylated cyclohexane causes a chemical-shift increase of about 2-2.5 ppm (79).

The fact that essentially no effect is observed in the norbornane system when the substituent is trans to the fluorine, strongly rules out σ-bond inductive effects as being relevant. Dewar would perhaps care to invoke field effects, reminiscent of the Kirkwood-Westheimer treatment (80), as being responsible for the observed changes (81). In the opinion of this writer, the observed effects in fluorine shifts are too large to be the result of "field effects." Further, the failure of simple models, such as Feeney's electric field model, to adequately reproduce experimental results discourages one from accepting Dewar's proposition.

Accordingly, an attempt was made to reproduce the observed vicinal effects by employing a more sophisticated treatment. The Pople treatment that was sketched out in Section II was put to work; Pople's expression for the trace of the shielding tensor was programmed for computation, employing both the average-energy version and the more complete expression. To begin with, the formalism was tested by estimating the shielding parameter for a series of miscellaneous

fluorides. In the estimation of the individual diamagnetic and paramagnetic terms, the $\langle r^{-1} \rangle$ and $\langle r^{-3} \rangle$ factors were evaluated by making use of Slater's rules for computing the effective nuclear charge (82).* For atoms where the diamagnetic term is the only contribution to the shielding, one can assess the value of Slater's rules by comparing the shielding calculated in this way with the shielding calculated by first computing $\sum_k \frac{1}{r_k}$ (where k runs over all electrons) with refined Hartree-Fock wavefunctions. A comparison of the results is given in Table 12.

In general, Slater's rules function very well for estimating atomic shielding. In a molecule, of course, the numbers in Table 12 will be modified according to the Pople formalism by appropriate charge densities. Alternatively, it has been suggested that σ_d for a nucleus in a molecule can be estimated from the value for the free atom according to the expression (83),

$$\sigma_d(N) = \sigma_d(\text{atom}) + \frac{e^2}{3\,mc^2} \sum_{N' \neq N}{}' \frac{Z_{N'}}{R_{NN'}} \qquad \text{(IV-50)}$$

where $Z_{N'}$ is the nuclear charge of an atom other than that whose shielding is being computed, and $R_{NN'}$ is the distance between atom N and the other nucleus.

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* Karplus and Pople used an expression of the form $Z_N' = Z_N - 0.35(\rho_N - 1)$ to allow for the fact that the local density on atom N in a molecule may be different from that in a neutral atom: M. Karplus and J. A. Pople, J. Chem. Phys., 38, 2803 (1963).

Table 12. Diamagnetic Shielding in Atoms

Atom	Slater's rules (ppm)	Hartree-Fock[a] (ppm)	Difference[e]
^{1}H	17.75	17.75, 17.75	0.00
^{7}Li	101.62	101.45, 101.42, 94.66[b]	-0.17
^{9}Be	148.66	149.26, 149.28, 149.61[b]	0.60
^{11}B	201.46	201.99, 199.33	0.53
^{13}C	260.03	260.74, 260.75, 265.8[c]	0.71
^{14}N	324.38	325.47, 325.18	1.09
^{17}O	394.45	395.11, 395.12	0.66
^{19}F	470.38	470.71, 463.63, 478.31[d]	0.33

[a] The first value listed is from G. Malli and S. Fraga, Theor. Chim. Acta, 5, 275 (1966), the second from the paper by Dickinson (see reference 4).

[b] W. A. Goddard III, J. Chem. Phys., 48, 1008 (1968).

[c] K. M. S. Saxena and P. T. Narasimhan, J. Chem. Phys., 42, 4304 (1965).

[d] T. W. Sidwell and R. P. Hurst, J. Chem. Phys., 37, 203 (1962).

[e] Values formed by subtracting numbers in the second column from the first entry in the third column.

Calculations were carried out using two sources of approximate wavefunctions: the extended Hückel routine exploited by Hoffmann (84, 85), and the CNDO/2 method developed by Pople, Santry and Segal (86, 87). Calculations carried out with the first source of wavefunctions utilized a program written by G. A. Petersson (88); for the second set

of calculations a program was kindly provided by Dr. R. J. Pugmire (89). In both sets of calculations, the basis orbitals are Slater orbitals.

Basically, the two methods are similar in spirit. A major difference is that in the CNDO/2 method, in contrast to the extended Hückel treatment, the required diagonal and off-diagonal matrix elements are obtained by an iterative procedure. In addition, the CNDO/2 treatment takes some account of electron-electron repulsions; the extended Hückel treatment ignores this effect.

The results of the calculation of the diamagnetic, paramagnetic and total shielding for several fluorides are shown in Table 13. Column 5 gives a value for the "experimental" shielding parameter. This is arrived at in the following manner: for HF the diamagnetic contribution has been computed rather accurately to be 482 ppm (90). Ramsey has shown that the paramagnetic contribution for a diatomic molecule can be related to the spin-rotational tensor components of the molecule by the following expression (91, 92):

$$\sigma_p = \frac{e^2}{3mc^2}\left[\frac{h}{4M\beta_N^2 g_N}\sum_{\alpha} C_{\alpha\alpha} I_{\alpha\alpha} - \sum_{a}\frac{Z_a}{R_a}\right] \qquad \text{(IV-51)}$$

where Z_a and R_a are the charge and distance of the ath nucleus from nucleus N, M is the proton mass, β_N is the nuclear magneton, g_N is the nuclear g-factor, and $C_{\alpha\alpha}$ and $I_{\alpha\alpha}$ are the diagonal-components of the spin-rotation and moment-of-inertia tensors, respectively. The C's arise from the interaction of the nuclear spin $\vec{I}$ (symbol not to be

Table 13. ^{19}F Shielding in Several Fluorides

Compound	σ_d(calcd, ppm) ETH[a,b]	CNDO	σ_p(calcd, ppm) ETH[a,b]	CNDO	σ(calcd, ppm) ETH[a,b]	CNDO	σ(exp, ppm)[d]	Ref.	Ref.
NOF	478.0		-267.5		210.5		-631	93a	94a
F_2	459.6	423.9	-1106.2	-244.4	-646.6	179.5	-211	b	b
OF_2	468.1		-488.5		-20.4		-62	c	c
NF_3	472.1		-271.8		200.3		72	d, e	a
cis-FN=NF	474.6		-295.4		179.2		85	c, f	d
trans-FN=NF	473.6		-308.5		165.1		126	e, f	e
SF_6							166	b	
CH_3COF							171	g	
HCOF	475.0		-228.0		247.0		177	g	f
HNF_2							220	i	
F^*–CO_2CF_3							233	j	
CF_4	474.9	429.7	-164.3	-277.5	310.6	152.2	281	k	g
CH_3BF_2							287	l	

Table 13. (Cont'd)

Compound	σ_d(calcd, ppm) ETH[a,b]	CNDO	σ_p(calcd, ppm) ETH[a,b]	CNDO	σ(calcd, ppm) ETH[a,b]	CNDO	σ(exp, ppm)[d]	Ref.	Ref.
CH_3COOH							296	m	
$CH_2=CF_2$	475.1	416.7	-196.9	-317.5	278.2	99.8	306	g, h	h
$CH_2=CHF$	476.1	408.5	-193.5	-320.7	282.6	87.8	329	n	i
C_6H_5F	476.3	406.6	-190.6	-319.5	285.7	87.1	331[c]	m	j
BF_3	480.6		-77.8		402.8		345	b	k
trans-$CH_3CH=CHF$							347	o	
cis-$CH_3CH=CHF$	476.2	403.9	-186.9	-298.8	289.3	105.1	349	o	l
C_4F_8							359	p	
CH_2F_2	476.6	421.2	-156.5	-266.1	320.1	155.1	361	k	m
F–C≡N							373	p	
cis-CHF=CHF	476.2	390.3	-184.9	-138.3	291.3	252.0	386	q, r	n
trans-CHF=CHF	476.0	356.6	-184.3	-151.0	291.7	205.6	404	r	o
HF	473.5	428.9	-159.7	-232.6	313.8	196.3	414	90	p

Table 13. (Cont'd)

Compound	σ_d(calcd, ppm) ETH[a,b]	CNDO	σ_p(calcd, ppm) ETH[a,b]	CNDO	σ(calcd, ppm) ETH[a,b]	CNDO	σ(exp, ppm)[d]	Ref.	Ref.
CH_3CH_2F							431	93s	
H–C≡C–F	473.1	408.6	-223.2	-314.0	249.9	94.6	474	t	q
CH_3F	477.4	409.2	-146.5	-236.0	249.9	173.2	490	k	r

[a] The Slater orbital exponents were an "improved" set suggested by Duncanson and Coulson: W. E. Duncanson and C. A. Coulson, Proc. Roy. Soc. (Edinburgh), 62A, 37 (1944). Hydrogen was assigned an exponent of 1.150.

[b] The approximate Coulomb integrals were taken from the paper L. C. Cusachs and J. W. Reynolds, J. Chem. Phys., 43, S160 (1965). In equation 5 in the paper by these authors, the value of q was consistently taken to be 2.

[c] Chan and Dubin report a value of 334 ± 10 ppm: S. I, Chan and A. S. Dubin, J. Chem. Phys., 46, 1745 (1967).

[d] Recently, a somewhat similar list of shielding parameters for a few fluorides has appeared; these are consistently about 20-25 ppm downfield from the values given in Table 13: D. K. Hindermann and C. D. Cornwell, J. Chem. Phys., 48, 4148 (1968).

confused with $I_{\alpha\alpha}$ above) with the rotational angular momentum ($\vec{J}$) produced by end-over-end rotation of the molecule; this interaction shows up in the Hamiltonian as

$$\mathcal{H} = -h\,\hat{I}\cdot\underset{\sim}{C}\cdot\hat{J}. \qquad \text{(IV-52)}$$

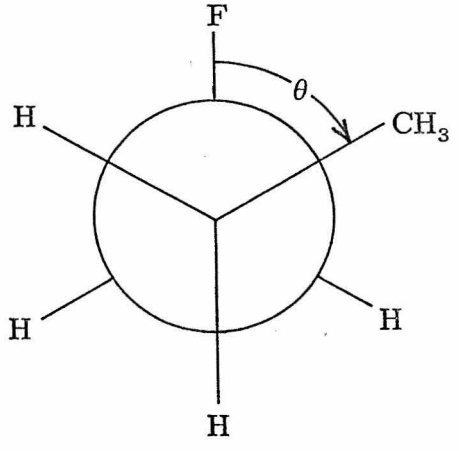
The C's can be experimentally determined; for HF the paramagnetic term is then calculated to be -68 ppm, giving a total shielding of 414 ppm.

All other fluorides can be experimentally related to HF; the references in column 6 of Table 13 relate to experimentally observed chemical shifts, and the references in column 7 refer to structural data for each molecule where this is available.

Some of the major experimental trends of fluorine shifts are reproduced in the calculations: molecular fluorine is predicted to lie far downfield from nearly everything else, whereas methyl fluoride is predicted to be at the other extreme; fluorine attached to a carbon bearing an unsaturated linkage is generally predicted to resonate lower than fluorine attached to a saturated carbon; fluorine attached to oxygen or nitrogen is predicted to resonate at lower field than fluorine attached to carbon. On the other hand, many discouraging features turn up in the data. Nitrosyl fluoride is not calculated to lie far downfield from molecular fluorine. This three-atom system is perhaps still small enough to permit quantum mechanical treatment at a more refined level. It has been suggested that a very low excitation energy is partly responsible for the observed antishielding (93a).

In many cases, the correct ordering among isomers is not reproduced; finally, chemical shifts work out to be rather smaller than the experimental values. An even smaller spread of values is predicted with the CNDO/2 wavefunctions, and on the whole, this method seems to perform no better or even slightly worse than the extended Hückel method (95).

To return to the original incentive for performing the calculations (p.146), it was decided to use extended Hückel wavefunctions and to carry out one additional set of calculations. It was felt that n-propyl fluoride (XVI), a "freely-rotating" ethane rotamer, might be a suitable system to use in simulating the effect of a methyl group on vicinal fluorine shielding.



(XVI)

The shielding in (XVI) was calculated for several values of the dihedral angle θ, and the results plotted; Figure 15 shows the plot that resulted. And indeed, these crude calculations suggest that shielding should be at a maximum when the fluorine and the methyl are cis, that there should be a minimum in the shielding, and that the shielding should again increase as θ tends to 180° (trans arrangement). Unfortunately, the calculated effects are somewhat smaller (ca. 2 ppm, maximum) than those observed in the norbornane system, and the curve does not dip even close to the estimated 120° in the norbornane system. This may be due in part to the fact that standard bond angles and distances were used in the n-propyl fluoride calculation rather than those appropriate to the more strained skeleton.

Examination of Tables 6-8 reveals that none of the compounds listed permits a test of the 180° point on the curve of Figure 15. To this end, the following test was devised: in 9-methyl-1,1-difluoro-trans-decalin the methyl group and the axial fluorine should lie in a coplanar, trans arrangement. The same situation would also obtain in the cis decalin, but use of the trans isomer would allow the measurement to be made at room temperature. Fluorination of trans-1-decalone gave the desired parent difluoride; the 9-methyl derivative (XVIII) was prepared by the scheme outlined below.

Isomers (XVII) and (XVIII) were not separated from each other; however, it is known that the trans ketone predominates in the methylation. Further, the difluoride present in major quantity showed no temperature dependence of its nmr spectrum. Table 14 shows

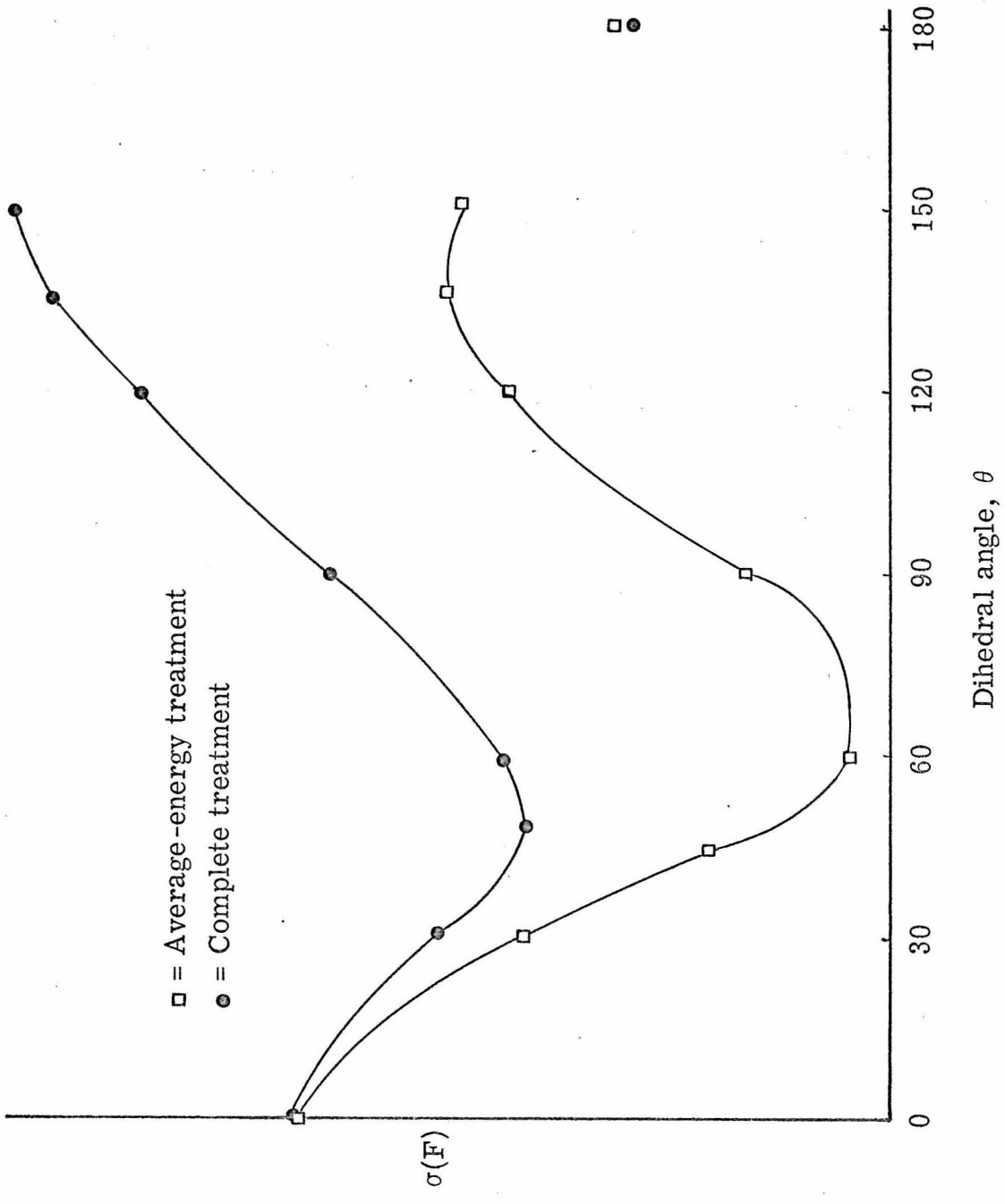
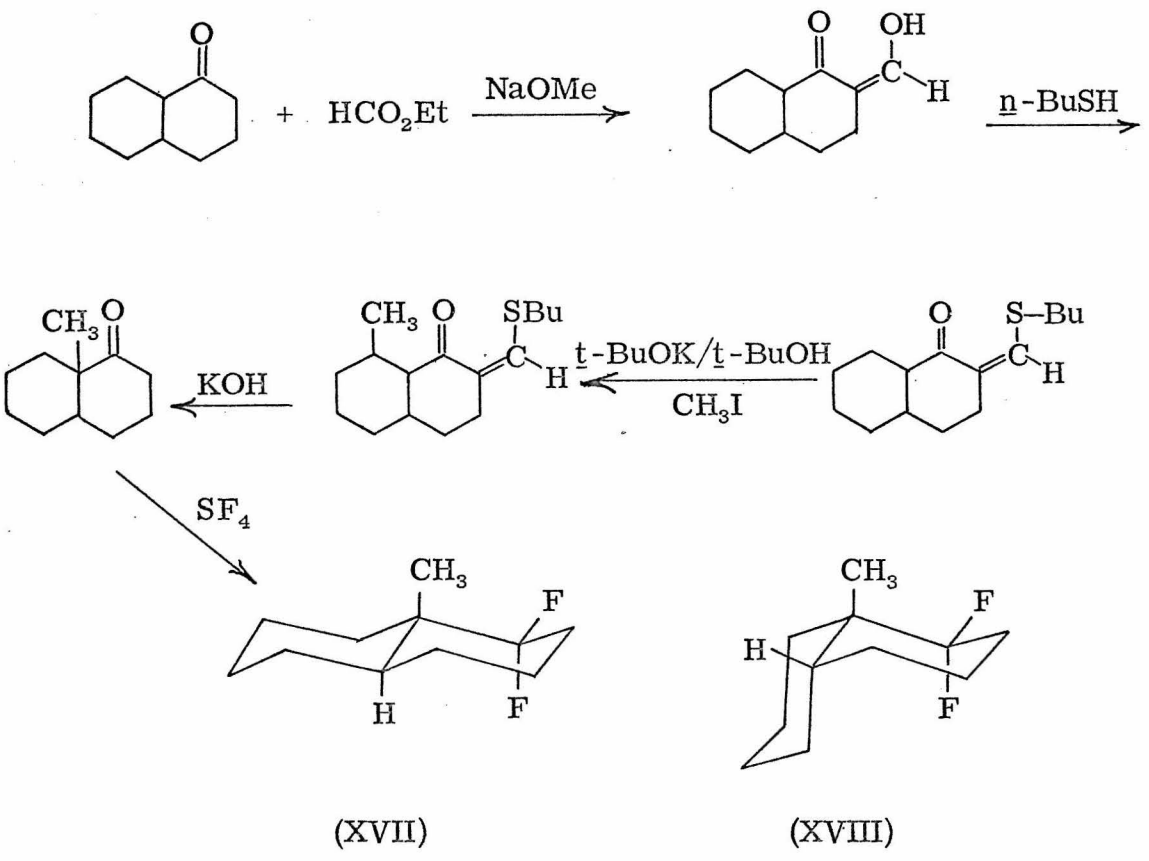


Figure 15. Plot of calculated ^{19}F shielding vs dihedral angle in n-propyl fluoride

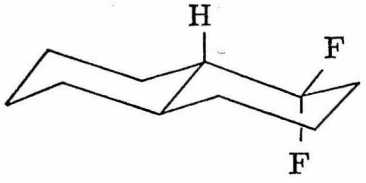
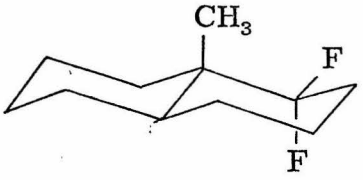


(XVII) (XVIII)

Figure 17. Synthesis of 9-methyl-1,1-difluorodecalin (XVII)

the relevant data obtained with (XVII) and the parent gem-difluoride. It is assumed that the upfield signals, which are broad (ca. 60 Hz), belong to the axial fluorine in both cases. The results clearly indicate that for dihedral angles of 60° and 180°, the effect of a methyl substitution is an upfield shift of about 10 and 15 ppm, respectively.

Table 14. ^{19}F Data for Two 1,1-Difluoro-trans-decalins

Compound	Upfield F[a]	Downfield F[a]	J_{FF}[b]
	48.1	63.4	237
	33.0	53.8	236

[a] Data in ppm downfield from internal C_6F_6.

[b] Data in Hz at 56.4 MHz.

It was anticipated that in endo-5-methyl-2,2-difluoronorbornane (see Table 11) the effect of the methyl substitution should be to preferentially alter the shielding of the endo fluorine; the data show that indeed the exo fluorine is but slightly affected, whereas the endo fluorine is moved upfield by 2 ppm, relative to the parent material. It came as a surprise to find that in the endo-6 isomer, where now the methyl group is significantly closer to the endo fluorine, both fluorine nuclei resonate at lower field (relative to 2,2-difluoronorbornane) and that the exo fluorine is the more strongly affected!

An explanation is not easily forthcoming, but it may be recalled from Table 6 that the effect of placing a methyl group in the 9-position of 2,2-difluoro-cis-decalin is to shift the axial fluorine upfield. In this respect, the effect in the norbornane situation resembles a 1,3-diaxial interaction in a cyclohexane or decalin system. Accordingly, it may be predicted that in 7,7-dimethyl-2,2-difluoronorbornane the effect of the syn-7-methyl group should be to shift the exo fluorine downfield; a 5-ppm downfield change is observed. To determine if much of this change is actually due to the anti-7-methyl group, anti-7-methyl-2,2-difluoronorbornane (X) was prepared and examined (see Figure 16). The spectral parameters for this compound are similar to those of 2,2-difluoronorbornane. It should also be remarked that, as with endo-6-methyl-2,2-difluoronorbornane, it is the more distant fluorine that is strongly affected by the methyl substituent in the 7,7-dimethyl case. This behavior is not encountered in the decalin and cyclohexane systems.

It is interesting to inquire why opposite behavior is observed in the shielding of the endo fluorine in the endo-5- and endo-6-methyl-2,2-difluoronorbornanes. With carbon-13 shielding, Grant has suggested that, other things being equal, the observed changes are caused by a steric interaction or perturbation on the carbon of interest and that this perturbation is a simple function of distance and angle as shown below (96).

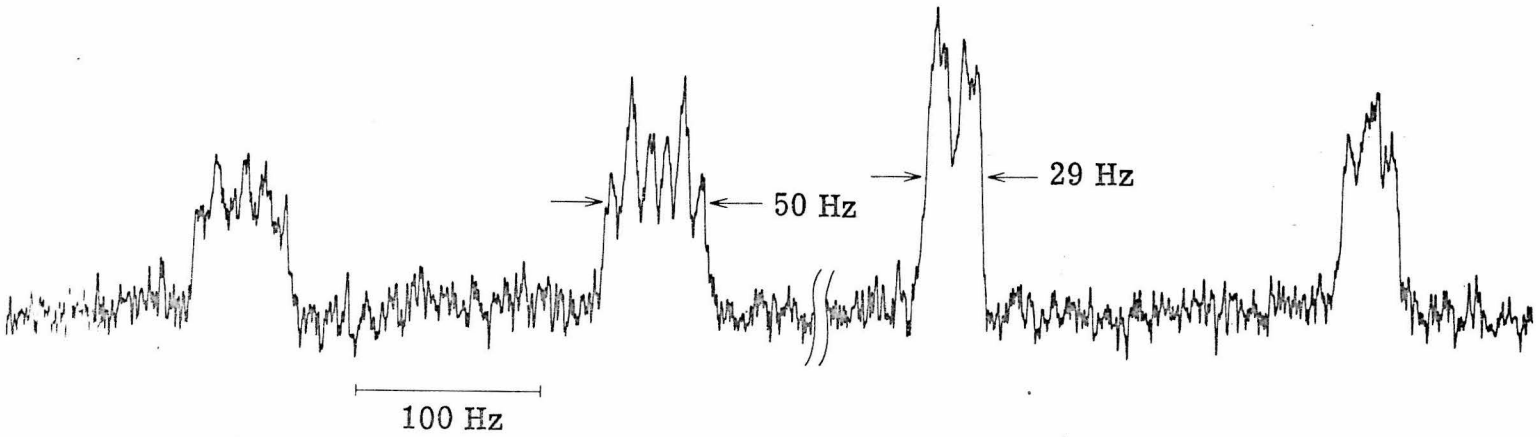
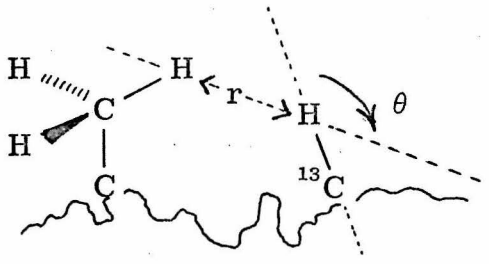


Figure 16. ^{19}F Nmr spectrum of anti-7-methyl-2,2-difluoronorbornane



$$\sigma(\text{C-13}) = f(r, \cos\theta)$$

This argument was generated for perturbation by a neighboring methyl group on a hydrogen attached to the nucleus of interest. It is doubtful whether these ideas could apply when the magnetic nucleus is univalent (fluorine) and when the substituent is monatomic (such as chlorine). Nevertheless, it seems plausible to suppose that in the endo-5 and endo-6 isomers, the methyl groups do affect the circulation of the nonbonded fluorine electrons differently. It is difficult to see exactly why this should be so, and the difficulty becomes even more apparent when one realizes that to properly evaluate the situation one is required to make rather tricky deductions about the conformations of the methyl groups. In this respect, a methyl group is clearly a complex substituent compared to a halogen.

V. Conclusions

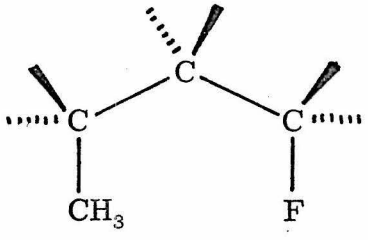
We may begin discussion of the "final solution" to those problems which lay before us by pointing out the salient results of the present study:

(1) Introduction of a methyl substituent β to a fluorine causes a change in the shielding, which is probably not due to an inductive effect. The fall-off factor is probably small enough so that only 1 or 2 ppm can legitimately be ascribed to a σ-bond polarization. For example, replacement of a hydrogen in HCF_2-CF_2H with a CF_2H group causes an upfield shift of one of the terminal fluorines of only 1 ppm (93s, 97).

(2) The magnitude of the effect of the β methyl group is dependent on the dihedral angle between it and the fluorine nucleus. The experimental curve of shielding vs. angle appears to have maxima at the extremes (0° and 180°) and a minimum near 120°. Effects at 60° are still large. That such a curve should be observed is predicted by crude quantum mechanical calculations.

(3) No instances have been found where the β methyl group causes a large downfield shift of the fluorine resonance.

(4) Introduction of a methyl substituent γ to a fluorine can cause either a slight upfield shift or a large downfield shift. The latter effect is found both in flexible and in rigid systems, and seems to occur when the following arrangement of atoms obtains:



Again, σ-bond polarization cannot likely account for this effect; rather, a more specific interaction between the substituent and the nonbonded electrons on the fluorine seems plausible. Additional data pertaining to the dependence of shielding on geometry could be obtainable by examination of the spectra of exo-6-methyl-2,2-difluoronorbornane, 4-methyl-2,2-difluoronorbornane and exo-6 and endo-6-methyl-2,2-difluorobicyclo[2·2·2]octane.

It is clear that for anything except substitution at the α position, it is dangerous to rely on simple models to rationalize fluorine chemical shift behavior. Simple models wherein one takes into account inductive effects, field effects, steric repulsion, etc. cannot be used as freely in accounting for magnetic phonomena as is done for chemical phenomena. Consider, for example, the fact that axial fluorines and endo fluorines are generally upfield from their equatorial and exo analogs. Although it is true that structurally the former are the more sterically congested, this does not itself constitute an explanation. The fact that many effects observed in flexible systems are paralleled in the rigid norbornane system, suggests that one must seek explanations which incorporate elements common to both.

Better calculations than those done in this work are needed before one can being to lay his finger on the real cause of the angular β effect. It is clear that other substituents besides a methyl group should be introduced into flexible and rigid systems in order to determine whether or not any of the trends observed in the present work are peculiar to the methyl group. Finally, it seems clear that any trends whatsoever that are observed in fluorine shielding can only be reproduced quantitatively by means of a mathematical treatment that is as close as possible to a strict application of the Ramsey formalism.

VI. Experimental Section

All melting points and boiling points are uncorrected; the former were taken on a Büchi melting-point apparatus. Infrared spectra were taken on either a Perkin Elmer 237 Infracord or a Model 237 grating spectrophotometer, and the proton nmr spectra were obtained with a Varian A-60A spectrometer. Proton chemical shifts are generally reported in ppm downfield from internal tetramethylsilane (TMS) (δ 0.00). All fluorine nmr spectra were obtained with a Varian A-56/60A spectrometer, and chemical shifts are reported in ppm, generally downfield from hexafluorobenzene. Vpc analyses and separations were carried out with a Varian Aerograph Autoprep Model 700 instrument. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

2,2-Difluoronorbornane. Five grams (0.045 mole) of norcamphor was dissolved in 25 ml of methylene chloride and the solution placed in a stainless-steel bomb. From a syringe was added 0.82 ml of water. The bomb was cooled in a dry ice--acetone bath and 33.4 g (0.309 mole) of sulfur tetrafluoride was condensed in. The bomb was sealed and shaken in a Parr rocker at room temperature for 15-16 hours.

At the end of this time the bomb was vented and the contents poured into a separatory funnel. The light-tan colored solution was shaken twice with 10% sodium bicarbonate, once with water, and once with saturated sodium chloride solution. After the methylene chloride

extract was dried over anhydrous sodium sulfate, it was distilled from a 50-ml micro flask at atmospheric pressure. The product came over at 115°, but because it tended to solidify in the condenser, the water cooling was stopped and the material driven through to the receiver with a flame. There was obtained 3.3 g (55%) of a white, camphoraceous solid, mp 73°.

The infrared spectrum showed strong bands at 2990, 2890, 1480, 1460, 1440, 1350, 1315, 1185, 1140, 1105, 1065, 985, 895, and 850 cm^{-1}. In the proton nmr spectrum there appeared unresolved multiplets at δ 1.1-1.9 and at δ 2.2-2.6. A carbon-13 nmr spectrum of the difluoride, taken by Dr. Frank Weigert of this laboratory, revealed that the two carbon-fluorine coupling constants were unequal.
Anal. Calcd for $C_7H_{10}F_2$: C, 6364; H, 7.57; F, 28.79. Found: C, 63.51; H, 7.55; F, 28.66.

exo-2-Methyl-endo-2-norbornanol. The procedure of Sauers was used (98). In a 500-ml, three-necked flask, fitted with magnetic stirrer, gas-inlet tube and condenser was placed 60 ml of ether and 8.1 g (0.338 mole) of magnesium turnings. From a funnel was added a solution of 47.8 g (0.336 mole) of iodomethane in 60 ml of ether. When the addition was complete, the solution was stirred for another two hours under nitrogen at room temperature. Then from the funnel was added dropwise a solution of 18.3 g (0.166 mole) of norcamphor in 120 ml of ether. The contents were then stirred at room temperature overnight.

The gray suspension was poured onto a mixture of 200 g of ice and 30 g of ammonium chloride in 60 ml of water and worked up in the usual manner. The ether layer was concentrated at a rotary evaporator and the residual oil distilled. The product came over as a colorless oil, bp 83-4° (20 mm)(lit. (98) 66-67° (9.5 mm)), and with a freezing point somewhere in the range of 5-30°. The yield was 16.7 g (80%).

The infrared spectrum showed a broad peak centered at about 3400 cm^{-1}, while the nmr spectrum showed a sharp methyl singlet at δ 1.33.

1-Methyl-exo-2-norbornyl Acetate. The procedure of Beckmann, Schaber and Bamberger was used (99). A solution of 16.3 g (0.121 mole) of exo-2-methyl-endo-2-norbornanol, 36 ml of acetic acid and 20 drops of concentrated sulfuric acid was placed in a 100-ml flask and stirred for 4.5 hours at 50-60°. The sweet-smelling solution was added to a mixture of water and ice in a large beaker and carefully neutralized with aqueous sodium bicarbonate. Ether was then added and the mixture worked up in the usual manner. There was obtained upon distillation 20.1 g (99%) of a very sweet-smelling oil, bp 98-100° (20 mm)(lit. (99) 90° (13 mm)); its infrared spectrum showed an intense carbonyl band at 1715 cm^{-1}.

1-Methyl-exo-2-norbornanol. In a 500-ml, three-necked flask fitted with magnetic stirrer, reflux condenser and dropping funnel was suspended 4.5 g of lithium aluminum hydride in 100 ml of dry ether.

From the funnel was added slowly a solution of 20.1 g (0.120 mole) of 1-methyl-exo-2-norbornyl acetate in 90 ml of ether with rapid stirring. After one hour the addition was complete; the solution was refluxed for 8.5 hours and then stirred at room temperature for 8.5 hours. The contents were then cooled in an ice bath and the excess reductant destroyed with 5% aqueous sulfuric acid. The ether layer was treated in the usual manner, concentrated and distilled to give 11.3 g of solid distillate, bp 95° (25 mm) (lit. (117) 90° (12 mm)).

The nmr spectrum showed the presence of two methyl singlets, thus indicating incomplete Wagner-Meerwein rearrangement. The entire amount of material was therefore resubjected to rearrangement followed by hydride reduction. This time there was obtained 10 g (61% based on unrearranged alcohol) of solid alcohol possessing one methyl singlet at δ 1.0.

1-Methylnorcamphor. Jones reagent was prepared by first dissolving 26.7 g of chromium trioxide in 23 ml of concentrated sulfuric acid in an ice bath, and then adding 77 ml of water to make the volume about 100 ml and the concentration of chromic acid about 4M (100). Acetone was purified by distillation from potassium permanganate.

A solution of 10 g (0.080 mole) of 1-methyl-exo-2-norbornanol in 135 ml of purified acetone was cooled to 0-5° in an ice bath. From a funnel was added 35 ml of Jones reagent over a period of 3-4 minutes; oxidation began immediately as evidenced by the formation of green chromium (III) salts. After being stirred in the bath for 10 minutes more, the solution was poured into one liter of water. About one

pound of sodium chloride was stirred in to help salt out the organic material. The resulting mixture was then extracted several times with ether, and the ether washed and dried.

The bulk of the ether was distilled at atmospheric pressure from a 250-ml flask. The remaining light-yellow oil was transferred to a 50-ml micro flask and distilled under nitrogen. 1-Methylnorcamphor came over as a clear, colorless liquid, bp 73-74° (20-25 mm) (lit. (118) 54-55° (9 mm)). The yield was 6.3 g (57%).

The infrared spectrum showed a carbonyl band at 1725 cm^{-1}; the nmr spectrum showed a sharp methyl singlet at δ 1.15.

The semicarbazone was prepared and crystallized from water; it had mp 213-214° (lit. (98) 212-213°).

The 2,4-dinitrophenylhydrazone was prepared and crystallized from methanol; it had mp 162°.

1-Methyl-2,2-difluoronorbornane. In a stainless-steel bomb was placed a mixture of 8.0 g (0.065 mole) of 1-methyl-norcamphor, 1.75 ml (0.097 mole) of water and 30 ml of methylene chloride. The contents were cooled to -70° and 50.0 g (0.463 mole) of sulfur tetrafluoride was condensed into the cylinder. The contents were then shaken at room temperature for three days.

The resulting dark, vile liquid was shaken successively with 10% aqueous sodium bicarbonate, water and brine, then dried. Distillation at aspirator pressure gave a first fraction of 0.9 g of a volatile, waxy solid, mp 45-46°, followed by a second fraction, 3.4 g, which was partly solid and partly liquid and which VPC subsequently indicated to

be about half difluoride. The total yield is therefore 2.6 g (28%).

An infrared spectrum of the waxy solid (first fraction) showed strong bands at 2950, 2870, 1455, 1340, 1320, 1310, 1175, 1160, 1145, 1085 (doublet), 1035, 980 and 895 cm^{-1}. In the nmr spectrum the methyl signal appeared as a singlet at δ 1.15.

Anal. Calcd for $C_8H_{12}F_2$: C, 65.75; H, 8.22; F, 26.03. Found: C, 65.56; H, 8.22; F, 25.85.

On a previous occasion when fluorination was attempted at 70-75°, there was isolated a 25% yield of a white, crystalline solid, mp 90-93°, which analyzed for 41.33% fluorine, indicating it to be a trifluoride.

exo-3-Methylnorcamphor. A 500-ml, three-necked flask was fitted with high-speed stirrer and two Friedrich condensers. Attached to one condenser was a gas-inlet tube, and to the other a calcium chloride drying tube. A solution of 20 g (0.182 mole) of norcamphor in 300 ml of dry ether was placed in the flask and from a powder funnel was quickly added 10.5 g (0.270 mole) of finely divided sodium amide. Vigorous stirring was begun at reflux temperature while a slow stream of nitrogen was passed through the system to sweep out the ammonia formed. After one hour the stirring was stopped and the dirty, pea-green suspension of enolate was decanted from unreacted sodium amide and added directly to a stirred mixture of 258 g (1.82 moles) of methyl iodide in an equal volume of ether. An immediate white precipitate formed; the suspension was stirred and heated at reflux under nitrogen to complete the reaction. After nine hours, the cooled white suspension was added to ice in a one-liter beaker, the

layers separated, and the ether layer treated in the usual manner. Distillation gave 10.7 g (47%) of clear, colorless exo-3-methylnorcamphor, bp 90-91° (25mm) (lit. (101) 67° (14 mm)).

The infrared spectrum showed bands at 3015, 2965, 2875, 1740 and 1460 cm^{-1}. In the proton nmr spectrum there was broad adsorption from δ 1.3 to 2.6. The methyl group appeared as a doublet centered at δ 1.05 with a splitting of 7 Hz. Another doublet of smaller intensity was also present, presumably due to the endo-epimer. A carbon-13 spectrum was taken by Dr. Frank Weigert. The carbonyl region showed two signals in the approximate ratio 5-10:1.

exo-3-Methyl-2,2-difluoronorbornane. In the bomb was placed 6.95 g (0.056 mole) of exo-3-methylnorcamphor, 1.1 ml (0.061 mole) of water and 30 ml of methylene chloride. The contents were cooled to -70° in a dry ice--acetone bath and 62.0 g (0.574 mole) of sulfur tetrafluoride was condensed into the solution. The bomb was then heated to 75° and shaken for 27 hours.

The dark, red-brown contents were worked up as described before, and after distillation there was obtained 4.1 g of a yellow distillate. This consisted of one major component and three minor ones; the major one was removed by preparative VPC as a clear, colorless liquid, weighing 3.2 g (39%). The analytical boiling point was 125-126°.

The infrared spectrum showed strong signals at 2975, 1460, 1335, 1180, 1135 (doublet), 1115, 1090 and 980 cm^{-1}. In the proton spectrum the methyl signal appeared as a doublet of doublets centered

at δ 1.0 and having coupling constants J_{HH} = 7.2 Hz and J_{HF} = 2.8 Hz.

Anal. Calcd for $C_8H_{12}F_2$: C, 65.75; H, 8.22; F, 26.03. Found: C, 65.66; H, 8.24; F, 25.77.

endo-3-Methylnorcamphor. The route used was essentially that of Alder and Grell (102). 3-Methylene-2-norbornanone (Aldrich) was examined spectroscopically: the infrared spectrum showed a carbonyl peak at 1750 cm^{-1}, an olefin peak at 1660 cm^{-1}, and vinyl peaks at 910 and 940 cm^{-1}. The proton magnetic resonance spectrum showed complex absorptions at δ 1.2-3.2, and what appeared to be a set of two singlets at δ 5.15 and δ 5.7. Fine splitting of the order of 0.8 Hz could be seen when these peaks were expanded.

A solution of 19.5 g (0.160 mole) of 3-methylene-2-norbornanone in a mixture of 8 ml chloroform and 160 ml absolute ethanol (103) plus one teaspoonful of W2 Raney nickel was shaken under a hydrogen pressure of 20 psi for one hour. The suspension was then filtered and washed (caution!). The pea-green filtrate was concentrated at atmospheric pressure to a volume of 60-80 ml and then transferred to a 100-ml micro flask. A few ml of triethylene glycol was added as a chaser and the solution distilled to give 14.7 g (74%) of clear, colorless endo-3-methylnorcamphor, bp 85-86° (20 mm) (lit. (102) 68-69° (11 mm)).

The infrared spectrum showed strong carbonyl absorption at 1740 cm^{-1} and almost no –OH absorption. In the proton magnetic resonance spectrum the methyl group appeared as a doublet centered at δ 1.0 and with a splitting of 7 Hz. The carbonyl portion of the carbon-13 spectrum was scanned by Dr. Frank Weigert; only one

signal was apparent, indicating a high degree of stereospecificity in the hydrogenation.

endo-3-Methyl-2,2-difluoronorbornane. A mixture of 14.9 g (0.120 mole) of endo-3-methylnorcamphor, 3.6 ml (0.200 mole) of water and 50 ml of methylene chloride was placed in the bomb and cooled to -70°. Then 91.0 g (0.840 mole) of sulfur tetrafluoride was condensed in, and the contents heated at 70° for 24 hours.

The resulting brown mixture was shaken successively with 10% aqueous sodium bicarbonate, water and brine, then dried. Distillation of the brown extract gave 2.1 g of unreacted ketone and 1.8 g (10%) of crude difluoride. Purification by preparative VPC resulted in a white, crystalline solid, mp 53-54°.

The infrared spectrum displayed bands at 2960, 2870, 1475, 1460, 1445, 1350, 1330, 1175, 1150, 1135, 1100, 1075, 1040, 1020, 980 (doublet), 940, 920 and 840 cm^{-1}. In the proton nmr spectrum the methyl signal appeared as a doublet of doublets, centered at δ 0.94 and having coupling constants J_{HH} = 6.8 Hz and J_{HF} = 2.4 Hz.

Anal. Calcd for $C_8H_{12}F_2$: C, 65.75; H, 8.22; F, 26.03. Found: C, 65.99; H, 8.35; F, 25.84.

3,3-Dimethyl-2,2-difluoronorbornane. A mixture of 8.8 g (0.064 mole) of camphenilone, 1.25 ml (0.070 mole) of water and 50 ml of methylene chloride was placed in the bomb. Sulfur tetrafluoride (73.8 g, 0.683 mole) was added in the usual manner and the contents were shaken at 90° for 24 hours.

The dark mixture was removed from the bomb and shaken successively with 10% aqueous sodium bicarbonate, water, and saturated sodium chloride solution. Distillation of the dried solution produced a white, crystalline fraction which VPC showed to be mostly unreacted ketone plus a small amount of a minor component. This component was isolated by preparative VPC; the yield of crystalline difluoride, mp 95-97°, was 0.8 g (8%).

The infrared spectrum showed strong bands at 2975, 1465, 1330, 1160, 1130, 1115, 1075, 1050, 1030 and 990 cm^{-1}. In the proton spectrum there appeared a doublet centered at 61.6 Hz from TMS and having a coupling constant of 8.2 Hz, and a singlet at 60.7 Hz from TMS.

Anal. Calcd for $C_9H_{14}F_2$: C, 67.50; H, 8.75; F, 23.75. Found: C, 67.62; H, 8.97; F, 23.27.

endo-5-Carboxy-2-norbornene. Dicyclopentadiene was freshly cracked and stored in the freezer until ready for use. Acrylic acid was distilled before use.

In a one-liter flask was placed a solution of 99 g (1.37 mole) of acrylic acid in 85 ml of dry ether. The flask was set in a bath of cool water, a magnetic stirrer and reflux condenser were attached, and from a dropping funnel was added with stirring 105 g (1.60 mole) of cyclopentadiene monomer. When addition was complete, the bath was removed and stirring was continued. The heat of the reaction caused the mixture to heat to the reflux temperature, but occasional tempering by short periods of cooling prevented matters from initially getting

out of hand. The solution was then stirred at room temperature for 27 hours.

The clear, colorless solution was distilled at aspirator pressure under argon. There was obtained 152 g (80%) of clear, colorless oil, bp 143-144° (27 mm) (lit. (104) 132-134° (22 mm)).

The infrared spectrum showed broad absorption in the region 2500-3500 cm^{-1}, and strong bands at 1710, 1640 cm^{-1}.

endo-5-Hydroxymethyl-2-norbornene. To a stirred suspension of 42 g (1.10 mole) of lithium aluminum hydride in 400 ml of dry ether was added a solution of 100 g (0.72 mole) of endo-5-carboxy-2-norbornene in 400 ml of ether. The mixture was refluxed for 14.5 hours, then the excess hydride was decomposed by adding 100 ml of water followed by 400 ml of 20% v/v aqueous hydrochloric acid. The ether solution was decanted from the white, insoluble precipitate and treated in the usual manner.

Solvent was stripped off at a rotary evaporator and the residue distilled at reduced pressure. The yield of clear, colorless endo-5-hydroxymethyl-2-norbornene was 68.6 g (76%). The infrared spectrum showed strong absorption at 3450 and 3645 cm^{-1}, and the complete absence of any carbonyl absorption.

endo-5-Brosylmethyl-2-norbornene. To a stirred suspension of 66.3 g (0.534 mole) of endo-5-hydroxymethyl-2-norbornene in 180 ml of dry pyridine was added portionwise 192 g (0.751 mole) of p-bromobenzenesulfonyl chloride with ice-bath cooling. After the mixture was stirred

in the bath for one hour, the flask was stoppered and set aside in the icebox for 5 days (105).

The suspension was then poured into a mixture of 1.5 liters of ice water and 125 ml of concentrated hydrochloric acid. It was extracted twice with 400-ml portions of ether and worked up. The ether was dried over sodium sulfate and stripped off at a rotary evaporator leaving a white solid. This was slurried in cold methanol, filtered and dried. The yield was 160 g (87%) of brosylate. Strong bands at 1360 and 1175 cm^{-1} in the infrared spectrum were indicative of the $-O-SO_2-$ group.

endo-5-Methylnorbornene. A 1500-ml, three-necked flask was fitted with magnetic stirrer, dropping funnel and condenser. To 350 ml of ether in the flask was added with stirring 14.8 g (0.393 mole) of lithium aluminum hydride; ice cooling of the contents was done during this addition. Then from the funnel was added a solution of 67.6 g (0.197 mole) of endo-5-brosylmethyl-2-norbornene in 350 ml of ether. The suspension was then stirred and heated under reflux for 14 hours.

Excess hydride was destroyed by the addition of 20% aqueous hydrochloric acid, followed by filtration of the resulting suspension. The ether solution was treated in the usual manner and finally dried. Most of the solvent was distilled through a 12-inch column; the residue was then transferred to a 100-ml flask and distilled at atmospheric pressure. The yield of clear, colorless olefin, bp 113-114° (lit. (105) 114-115°), was 12.9 g (65%).

The infrared spectrum showed strong bands at 3060, 2950, 2860, 1450, 1360, 1340, 1320, 1240, 1140, 1000, 925, 900 (doublet) and 825 cm^{-1}. In the nmr spectrum there was a methyl doublet at δ 0.8 with J_{HH} = 6.5 Hz, a complicated set of signals at δ 1.0-2.8, and an approximate olefin sextet at δ 6.05.

endo-5- and 6-Methylnorcamphor. In a 300-ml, three-necked flask, fitted with magnetic stirrer, dropping funnel and reflux condenser, was placed 2.1 g (55.6 mmole) of sodium borohydride, 0.38 g of zinc chloride and 100 ml of dry ether. The mixture was stirred under nitrogen at room temperature for 5 hours.

Then from the funnel was added over 5 minutes a solution of 20.0 g (185 mmole) endo-5-methyl-2-norbornene in 15 ml of ether, followed by slow addition of a solution of 10.6 g (75 mmole) of boron trifluoride etherate in 20 ml of ether. The solution was stirred at room temperature for 3 hours and then heated under reflux for 2 hours (106).

The excess hydride was decomposed with 10 ml of water and the ether solution of the organoborane transferred to a 500-ml flask immersed in a cold water bath. Other a period of 30 minutes there was added with stirring 166 ml of Brown's reagent (107); when the addition was complete, the solution was stirred for one hour and then refluxed for 2 hours.

The layers were separated, the aqueous portion extracted with ether, and the combined ether solutions washed and dried. The solvent was stripped off and the residue fractionated at aspirator

pressure to give 9.0 g (39%) of ketonic material, bp 83-84° (20 mm). Analytical VPC showed this to consist of two major components and one minor component, the latter presumably being an inseparable mixture of exo-5- and exo-6-methylnorcamphor. Preparative VPC was carried out on a 20-ft Carbowax column at 180°, and although all three components still had close retention times, modest separation was achieved. The conditions were rather critical: below 180° the ketones apparently would not elute from the column, while above 180° they emerged in too close sequence. Injections could be no larger than about 100-125 μl. Analytical VPC of the two major, isolated components showed them to be better than 90% pure. Identification of the two isomers was made by comparison of the infrared spectra with those of authentic samples supplied by Professor J. A. Berson (108).

The infrared spectrum of the endo-5-isomer had strong absorptions at 2960, 1740, 1450, 1410, 1050 and 1000 cm^{-1}. In the proton nmr spectrum the methyl group appeared as a doublet centered at 71 Hz and with a J_{HH} of 6 Hz.

The infrared spectrum of the endo-6-isomer had strong absorptions at 2960, 1740, 1455, 1410, 1385, 1295, 1170, 1150, 1090, 100 and 910 cm^{-1}. In the proton nmr spectrum the methyl group appeared as a doublet centered at 67 Hz and with a J_{HH} of 6 Hz.

endo-5-Methyl-2,2-difluoronorbornane. In a stainless-steel bomb was placed 1.22 g (9.8 mmole) of endo-5-methylnorcamphor, 0.27 ml (15.0 mmole) of water and 15 ml of methylene chloride. The contents were cooled to -70° in a dry ice--acetone bath and 10.0 g (92 mmole)

of sulfur tetrafluoride was condensed into the bomb. The contents were shaken at 50-55° for 20 hours.

The resulting tan extract was then shaken successively with 10% aqueous sodium bicarbonate, water and brine to give a nearly colorless solution. The dried solution was concentrated somewhat and the difluoride isolated by preparative VPC on a Carbowax column at 135°; 600 μl-injections were made. The yield of clear, colorless endo-5-methyl-2,2-difluoronorbornane, freezing just below room temperature, was 770 mg (53%).

An infrared spectrum of the difluoride showed strong absorptions at 2960, 2890, 1470, 1455, 1440, 1380, 1350, 1305, 1250, 1190, 1155 (doublet), 1100 (doublet), 1065 (doublet), 1025, 1000, 965, 900 (doublet) and 870 cm^{-1}. The nmr spectrum showed a methyl doublet at δ 1.0 with J_{HH} = 6 Hz.

Anal. Calcd for $C_8H_{12}F_2$: C, 65.75; H, 8.22; F, 26.03. Found: C, 65.60; H, 8.30; F, 25.91.

endo-6-Methyl-2,2-difluoronorbornane. In a stainless-steel bomb was placed 1.32 g (10.6 mmole) of endo-6-methylnorcamphor, 0.30 ml of water (16.7 mmole), and 20 ml of methylene chloride. The contents were cooled to -70° in a dry ice--acetone bath and 13.5 g (125 mmole) of sulfur tetrafluoride was condensed into the bomb. The mixture was then shaken at 65-70° for 19 hours. After this time the cooled, tan solution was poured into a separatory funnel, shaken successively with 10% aqueous sodium bicarbonate, water, and brine. The almost colorless extract, after being dried, was concentrated somewhat and

then subjected to preparative vapor-phase chromatography. The difluoride was obtained as a colorless liquid, freezing just below room temperature. The yield was 430 mg (28%).

The infrared spectrum showed strong absorptions at 2970, 2370, 1460, 1365, 1340, 1320, 1305, 1270, 1190, 1145, 1105, 1080, 1020 and 1000, 955, 905 and 880 cm^{-1}. The proton nmr spectrum revealed the methyl signal to be a four-line pattern, centered at δ 1.15, and consistent with J_{HH} = 6 Hz and with a stereospecific coupling to one fluorine, J_{HF} = 4 Hz.

Anal. Calcd for $C_8H_{12}F_2$: C, 65.75; H, 8.22; F, 26.03. Found: C, 65.72; H, 8.30; F, 25.89.

7,7-Dimethyl-endo-2-norbornyl Acetate. The Diels-Alder adduct of spiro[4.2]heptadiene and vinyl acetate, obtained from Dr. F. C. Haupt, was examined by nmr spectroscopy. Cyclopropyl signals occurred at δ 0.42 and δ 0.9-1.2; an acetate methyl singlet was at δ 1.93, and olefinic signals occurred at δ 5.1-5.5 and δ 6.0-6.5.

Ethyl acetate was refluxed with a small quantity of acetic anhydride and then distilled from anhydrous potassium carbonate. A suspension of 2.65 g of platinum oxide in a solution of 17.2 g (0.097 mole) of spiro acetate in 85 ml of purified ethyl acetate was shaken in a Parr rocker for one day under a hydrogen pressure of 50 psi. The suspension was then filtered and the solvent distilled from the filtrate at atmospheric pressure, leaving 19.6 g of crude ester contaminated with a small amount of ethyl acetate. This mixture was used directly for the next step.

7,7-Dimethyl-endo-2-norbornanol. A slurry of 8.0 g (0.212 mole) of lithium aluminum hydride in 200 ml of ether was prepared in a 500-ml, three-necked flask. From a funnel there was added with stirring a solution of 19.6 g of crude 7,7-dimethyl-endo-2-norbornyl acetate in 100 ml of dry ether. The solution was stirred and refluxed under nitrogen for a day.

Excess hydride was destroyed with the minimum of 5% aqueous sulfuric acid and the salts were dissolved with 1:1 aqueous hydrochloric acid. The layers were separated, the aqueous portion extracted with ether, and the combined ether layers washed and dried. Removal of the solvent on a rotary evaporator left 7,7-dimethyl-endo-2-norbornanol as a light-yellow oil, 15.5 g, which was used directly for the next step without further purification.

Apocamphor. The crude 7,7-dimethyl-endo-2-norbornanol (15.5 g, 0.11 mole) was dissolved in 100 ml of reagent grade acetone and cooled to 0° in an ice bath. From a funnel there was added with good stirring over a period of 10 minutes 40 ml of Jones reagent. The suspension was stirred for 30 minutes more and the solution decanted from the green salts. The acetone extract was diluted with a liter of water, salted with one pound of sodium chloride, and then extracted several times with ether. The combined ether solutions were shaken with strong brine and dried over anhydrous calcium chloride.

The ether was removed in a rotary evaporator and the resulting oil distilled at aspirator pressure with a free flame. A waxy solid, 6.2 g (40%), was collected in the condenser. Analytical VPC showed

the presence of a major constituent (apocamphor) and two minor components. The desired fraction was collected by preparative VPC on a Carbowax column at 210°, making 750 μl-injections. The apocamphor so obtained was a white, crystalline solid, mp 105-109° (lit. (109) 108°).

The infrared spectrum had strong absorptions at 2960, 2880, 1740, 1455, 1415, 1395, 1375, 1315, 1275, 1180, 1110 and 1075 cm^{-1}. The proton nmr spectrum showed a very sharp methyl singlet at δ1.03.

7,7-Dimethyl-2,2-difluoronorbornane. In the stainless-steel bomb was placed 1.4 g (10.2 mmole) of apocamphor, 0.30 ml (16.7 mmole) of water and 20 ml of methylene chloride. The contents were cooled to -78°, the air evacuated from the cylinder, and then 12.0 g (111 mmole) of sulfur tetrafluoride condensed in. After being shaken at 75-80° for 22 hours, the mixture was recovered as a tan solution and worked up in the usual manner. Vapor-phase chromatography showed that while a new compound had been formed, most of the apocamphor remained unreacted. The pure difluoride was isolated by preparative VPC; the yield of white crystalline solid, mp 88-91°, was 120 mg (8%).

The infrared spectrum showed strong absorption at 2960, 1455, 1340, 1275, 1175, 1155, 1110, 1100, 1065 and 905 cm^{-1}. In the proton nmr spectrum the methyl signals appeared as two doublets centered at 62 Hz (J_{HF} = 1 Hz) and 69 Hz (J_{HF} = 3 Hz) from TMS.

Anal. Calcd for $C_9H_{14}F_2$: C, 67.50; H, 8.75; F, 23.75. Found: C, 67.38; H, 8.75.

Dibromocarbene and 1,3-Cyclohexadiene. This reaction was carried out under two slightly different conditions (110): (a) Commercial t-butyl alcohol was dried for use by distillation from calcium hydride; bromoform was shaken over calcium chloride and then distilled at aspirator pressure. To refluxing t-butyl alcohol (350 ml) was added carefully 17 g (0.436 g-atom) of potassium metal. When dissolution was complete, the solution was cooled to 0° in ice and a solution of 24.5 g (0.306 mole) of 1,3-cyclohexadiene in 100 ml of t-butyl alcohol was added. The temperature was maintained at 0° while from a dropping funnel there was added over 2 hours a solution of 74 g (0.292 mole) of bromoform in 50 ml of t-butyl alcohol. The suspension turned black after the initial addition of olefin, but as the bromoform was added the color changed to murky brown. The suspension was stirred for one more hour and the bath was then allowed to come to room temperature overnight.

The contents were then diluted with pentane. Water was added and after separation of the layers the aqueous portion was extracted with more pentane. The combined pentane fractions were washed with water and dried over sodium sulfate. The solvent was stripped off in a rotary evaporator leaving an orange oil; vacuum distillation of the residue gave 39.6 g (54%) of clear, colorless 7,7-dibromobicyclo-[4.1.0]hept-2-ene, bp 74° (1 mm).

(b) Commercial pentane was purified by stirring for one day with concentrated sulfuric acid and then distilling from phosphorus pentoxide. A one-liter, three-necked flask was charged with 300 ml of pentane and

49 g (0.437 mole) of solid potassium t-butoxide. The suspension was cooled to 0°, stirring was begun, and a solution of 20.2 g (0.253 mole) of 1,3-cyclohexadiene in 75 ml of pentane added. A solution of 74 g (0.292 mole) of bromoform in 50 ml of pentane was then slowly added from a dropping funnel with vigorous blade stirring. The addition required 3 hours.

The contents were stirred for an additional 1.5 hours; the layers were then separated, the aqueous portion extracted with more pentane, and the pentane extracts treated as before. Vacuum distillation gave 38.8 g (61%) of colorless olefinic dibromide, bp 71° (0.8 mm) (lit. (110) 68-70° (0.8 mm)).

The infrared spectrum showed bands at 3040, 3010, 2930, 2850, 1650, 1450, 1435, 1350, 1305, 1045, 840 and 680 cm^{-1}. The nmr spectrum consisted of a broad, complex signal at δ 1.8-2.1, and an unresolved multiplet at δ 5.9.

syn-7-Bromo-anti-7-methylnorbornene. The procedure of Skattebøl was followed (70). A 500-ml, three-necked flask was fitted with gas-inlet tube, rubber-septum cap and magnetic stirrer. The flask was charged with a solution of 75.0 g (0.297 mole) of the dibromobicycloheptene in 75 ml of dry ether. Stirring under argon was commenced while the solution was cooled to -78° in a dry ice--acetone bath. Then from a 50 ml-syringe was added 140 ml of 2.35 M methyllithium (0.329 mole) in ether over 70 minutes. After the addition was complete, the solution was stirred at -78° for 2 hours.

The light-yellow solution was then allowed to warm up to 0° and the excess methyllithium was destroyed with water. The layers were separated, the aqueous portion extracted with ether, and the combined ether extracts shaken successively with water and brine, then dried over anhydrous sodium sulfate. Distillation at the pump gave a major fraction boiling at 55° (5 mm) (lit. (70) 64° (8 mm)) and a minor fraction at 70° (1 mm). The yield of the first fraction, which came over partly as a liquid and as a solid, was 31.0 g (56%), and of the second fraction, 8.6 g.

The nmr spectrum of the major fraction (syn-7-bromo-anti-7-methylnorbornene) consisted of a multiplet centered at δ 1.0, a singlet at δ 1.7, a multiplet at δ 1.7-2.0, a broad unresolved signal at δ 2.8, and a triplet at δ 6.1. The infrared spectrum showed strong bands at 3070, 2980, 1470, 1440, 1380, 1330, 1300, 1160, 1125, 1110, 1060 and 700 cm^{-1}.

Reduction of syn-7-bromo-anti-7-methylnorbornene. In a 100-ml flask was placed 30.6 g (0.164 mole) of syn-7-bromo-anti-7-methylnorbornene and 41.4 g (0.142 mole) of tri-n-butyltin hydride (111). This was stirred at room temperature for one day; then an additional 22.6 g (0.078 mole) of tin hydride was added and the contents stirred for one more day. At the end of this time the solution was distilled directly at reduced pressure. There was obtained 15.9 g (90%) of clear, colorless, olefinic product, bp 50-52° (35 mm).

The nmr spectrum showed two triplets, centered at δ 5.9 and 6.1, consistent with a nearly 1:1 mixture of syn- and

anti-7-methylnorbornene. The infrared spectrum showed olefin bands at 3060, 1630 (weak) and 700 (doublet) cm^{-1}.

syn- and anti-7-Methylnorcamphor. A suspension of 2.65 g (0.070 mole) of sodium borohydride and 0.5 g of zinc chloride in 100 ml of dry ether was allowed to stir at room temperature under nitrogen for 6 hours. Then a solution of 15 g (0.139 mole) of a mixture of syn- and anti-7-methylnorbornene in 25 ml of ether was added rapidly from a funnel, followed by slow addition of a solution of 12.7 g (0.090 mole) of boron trifluoride etherate in 20 ml of ether. After being stirred for one hour at room temperature, the mixture was refluxed for 2 hours and then allowed to stand overnight at room temperature.

The excess hydride was decomposed with 15 ml of water and the ether decanted from the salts. To the ether solution, cooled in an ice bath, was added with stirring 150 ml of Brown's reagent (chromic acid), followed by one hour of stirring and one hour of refluxing.

The layers were separated, the aqueous layer extracted with ether, and the combined ether layers treated in the usual manner. Distillation gave 10.6 g (62%) of a colorless, sweet-smelling oil. Gas chromatography showed the product to consist of two components in a nearly 1 to 1 ratio. Separation was carried out on a portion of the mixture using a Carbowax column at 183°; injections were typically 350 μl.

The component of longer retention time was identified as anti-7-methylnorcamphor by comparison of its infrared spectrum with that of an authentic sample supplied by Professor J. A. Berson. Strong

bands were present at 2960, 2900 (doublet), 1740, 1475, 1445, 1405, 1380, 1295, 1250, 1180 and 1085 cm^{-1}. A methyl doublet appeared in the nmr spectrum, centered 57 Hz downfield from TMS and having a coupling constant of 6 Hz.

The infrared spectrum of the syn isomer displayed strong bands at 2960, 2880, 1735, 1450, 1410, 1385, 1250, 1235, 1170 (doublet), 1130, 1095, 1065, 1025, 955 and 855 cm^{-1}. In the nmr spectrum of this isomer the methyl doublet appeared 60 Hz downfield from TMS with a splitting of about 6 Hz.

Anal. Calcd for $C_8H_{12}O$: C, 77.42; H, 9.68. Found: C, 76.80; H, 9.65.

anti-7-Methyl-2,2-difluoronorbornane. In a stainless-steel bomb was placed 1.49 g (12 mmole) of anti-7-methylnorcamphor, 0.32 ml (18 mmole) of water and 20 ml of methylene chloride. After the contents were cooled to -78° and the air was evacuated, 10.0 g (92 mmole) of sulfur tetrafluoride was condensed in. The bomb was then shaken at room temperature for one day.

At the end of this time the straw-colored contents were emptied from the bomb, shaken successively with 10% aqueous sodium bicarbonate, water, brine, and then dried over sodium sulfate. The solution was concentrated somewhat and the difluoride isolated by preparative VPC on a Carbowax column at 185°; 700-μl injections were made, and the anti-7-methyl-2,2-difluoronorbornane (0.9 g, 52%) was collected as a clear, colorless liquid.

The infrared spectrum showed strong bands at 2960, 2880, 1475,

1445, 1385, 1330, 1310, 1250, 1235, 1180 (doublet), 1125, 1105, 1080, 1030, 1005, 980, 900, 870 and 845 cm^{-1}. In the proton nmr spectrum, the methyl resonance appeared as a doublet of doublets, centered 54 Hz downfield from TMS and having coupling constants J_{HH} = 7 Hz and J_{HF} = 1.6 Hz.

Anal. Calcd for $C_8H_{12}F_2$: C, 65.75; H, 8.22; F, 26.03. Found: C, 65.88; H, 8.23; F, 25.96.

trans-1-Decalone. A solution of 12.9 g (0.085 mole) of a mixture of cis- and trans-1-decalone in 400 ml of absolute methanol plus 4 ml of concentrated sulfuric acid was refluxed in a 500-ml flask for 18 hours. The cooled solution was diluted with a large volume of water and extracted several times with ether. The ether extract was then shaken with 10% sodium bicarbonate, followed by brine, and then dried. The solvent was stripped off at a rotary evaporator leaving an oil; distillation of this gave 10.5 g of clear, colorless trans-1-decalone, bp 75° (3.5 mm) (lit. (119) 107° (15 mm)).

The appearance in the infrared spectrum of a strong band at 910 cm^{-1} and only a weak band at 945 cm^{-1} indicated the presence of only a small amount of the cis-isomer (112).

1,1-Difluoro-trans-decalin. A stainless-steel bomb was charged with 7.1 g (0.047 mole) of trans-1-decalone, 1.25 ml (0.069 mole) of water and 50 ml of methylene chloride. The bomb was cooled in dry ice -- acetone and 33.0 g (0.306 mole) of sulfur tetrafluoride was condensed in. The contents were shaken at room temperature for 60 hours, after

which time the resulting dark, vile liquid was treated in the usual way. Distillation at a water aspirator gave 3.86 g (48%) of a straw-colored liquid, bp 85-90° (20 mm). Redistillation of a portion of this material gave 1,1-difluoro-trans-decalin as a light, pink-colored liquid, bp 89° (20 mm).

The infrared spectrum showed strong bands at 2930, 2850, 1450, 1380, 1355, 1325, 1280, 1265, 1170, 1150, 1135, 1100, 1090, 1080, 1040, 1020, 960, 945, 890, 845 and 810 cm^{-1}. The nmr spectrum showed only broad absorption from δ 0.8-2.2.

Anal. Calcd for $C_{10}H_{16}F_2$: C, 68.97; H, 9.13; F, 21.90. Found: C, 68.83; H, 9.07; F, 21.70.

2-n-Butylthiomethylene-1-decalone. A suspension of 52.5 g (0.973 mole) of dry, powdered sodium methoxide in one liter of reagent grade benzene was cooled to 0°; with blade stirring there was added a solution of 37.0 g (0.243 mole) of commercial α-decalone in 72.0 g (0.973 mole) of ethyl formate over a period of 15 minutes. The contents were stirred in the ice bath for 50 hours under a nitrogen blanket. Then 800 ml of ice water was added, the layers separated, the benzene layer washed once with dilute sodium hydroxide, and the combined aqueous layers washed once with ether. The aqueous solution was then divided in half and each half acidified with concentrated hydrochloric acid; a red immiscible layer appeared at the top of each solution. The mixture was extracted with ether, and the ether washed and dried. Removal of the solvent left 34.7 g (79%) of crude 2-hydroxymethylene-1-decalone as a dark oil (113).

This dark oil was dissolved in 150 ml of benzene along with 19.0 g (0.211 mole) of n-butyl mercaptan and 50 mg of p-toluenesulfonic acid; the solution was refluxed under nitrogen for 24 hours, during which time 4.5 ml of water was removed with a Dean-Stark trap. The resulting benzene solution was washed with 10% sodium bicarbonate, brine and dried over anhydrous sodium sulfate. The benzene was stripped off at a rotary evaporator and the red, oily residue vacuum distilled. 2-n-Butylthiomethylene-1-decalone came over as a light-yellow liquid, bp 155° (0.7 mm) (lit. (114) 129° (0.05 mm)), freezing just below room temperature into a nearly white solid (118). The yield was 41.0 g (84%).

The nmr spectrum showed continuous absorption in the range δ 0.8-3.0; a poorly resolved triplet appeared at δ 7.5. The infrared spectrum showed strong bands at 2930, 2860, 1720, 1630, 1580, 1450, 1230, 1180, 1140, 1060, and 890 cm^{-1}. Many of these bands were quite broad, indicative of the presence of tautomeric species.

9-Methyl-1-decalone. A solution of 39.1 g (1.00 g-atom) of metallic potassium in one liter of dried t-butyl alcohol was prepared under nitrogen. Then at room temperature there was added a solution of 70.0 g (0.278 mole) of 2-n-butylthiomethylene-1-decalone in 50 ml of t-butyl alcohol; the solution was stirred at room temperature for 15 minutes. The purple solution was chilled in ice, and through the condenser was added rapidly 176 g (1.25 mole) of methyl iodide; a pink suspension resulted. The suspension was cooled in ice water and stirred for 30 minutes, then refluxed for 6 hours.

At the end of this time the white suspension was cooled, transferred to a one-necked flask, and stripped of the t-butyl alcohol in a rotary evaporator. The slush was stirred with water to dissolve the salts, extracted with one liter of ether, and the extract washed successively with water and brine. After the solution was dried over sodium sulfate, the solvent was taken off at a rotary evaporator, leaving 9-methyl-2-n-butylthiomethylene-1-decalone as a dark oil which was used directly in the next step.

This oil was dissolved in a mixture of 200 ml of 25% aqueous potassium hydroxide and 200 ml of diethylene glycol and refluxed for one day under nitrogen. The clear, red solution was then transferred to a two-liter, three-necked flask and steam distilled. After 800 ml had been collected, the distillate was saturated with sodium chloride, extracted with ether and the ether solution washed successively with dilute potassium hydroxide, water and brine. The ether was dried over sodium sulfate, the solvent was taken off in a rotary evaporator and the resulting clear oil fractionated to give 21.7 g (47%, based on 2-n-butylthiomethylene-1-decalone) of 9-methyl-1-decalone, bp 100° (7 mm) (lit. (115) 86-88° (3 mm)).

The nmr spectrum showed two methyl singlets, centered at δ 1.1 and 1.2, of approximate intensities 1 to 2, respectively. In the infrared spectrum, strong bands occurred at 2940, 2870, 1700, 1450, 1380, 1315, 1240, 1155, 1105, 1040, 995 cm^{-1}.

9-Methyl-1,1-difluorodecalin. In a stainless-steel bomb was placed a mixture of 10 g (0.060 mole) of 9-methyl-1-decalone, 1.62 ml (0.090 mole) of water and 40 ml of methylene chloride. The contents were cooled in dry ice--acetone and 47.8 g (0.443 mole) of sulfur tetrafluoride was condensed in. The contents were then shaken at room temperature for 2 days.

The resulting thick, dark, vile mixture was cautiously shaken successively with 10% aqueous sodium bicarbonate, water, and saturated sodium bicarbonate, water, and saturated sodium chloride solution, and then dried over anhydrous sodium sulfate. Much of the resinous material present could be precipitated by diluting with 60-70° ligroin and boiling off most of the methylene chloride.

The still dark solution was transferred to a 50-ml micro flask and distilled at aspirator pressure. There was obtained 1.4 g (12%) of a straw-colored liquid, bp 83-84° (18 mm). Gas chromatography showed the presence of two volatile components in the ratio of about 3:1. These were collected together by preparative VPC on a Carbowax column at 205°.

The infrared spectrum showed strong bands at 2930, 2850, 1450, 1380, 1320, 1300, 1150, 1100, 1080, 1070, 1040, 1030, 980, 955, 895 and 845 cm^{-1}. In the proton nmr spectrum there were singlets at δ 1.0 and 1.1.

Anal. Calcd for $C_{11}H_{18}F_2$: C, 70.21; H, 9.57; F, 20.22. Found: C, 69.93; H, 9.55; F, 20.06.

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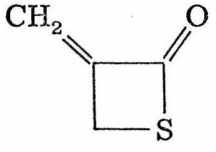
PROPOSITIONS

Proposition 1

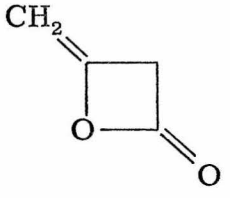
Abstract. The syntheses of two interesting compounds, one a small-ring compound and the other a strained aromatic hydrocarbon, are proposed.

Part A.

In previous years widespread interest in the synthesis and reactions of small-ring compounds has led to the discovery of numerous interesting compounds (1). A simple four-carbon molecule that is as yet unknown is α-methylene-β-propiothiolactone (I), whose oxygen analogue is isomeric with the well-known ketene dimer (II).



(I)

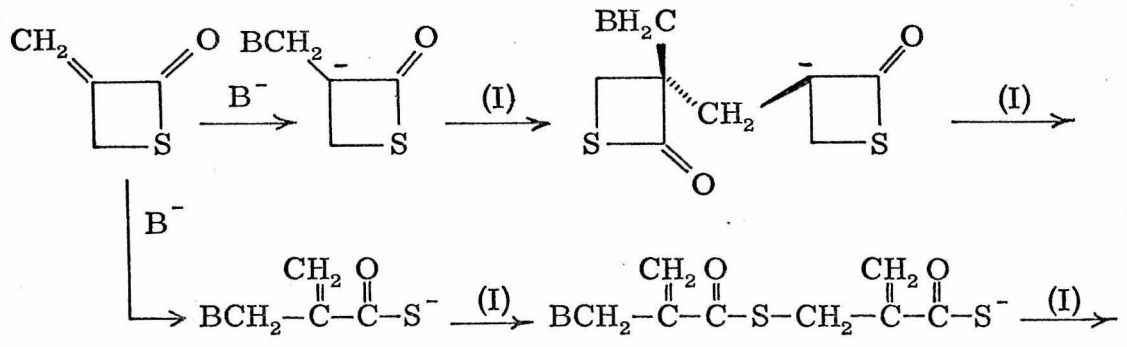


(II)

Thiolactone (I) should be an interesting compound for several reasons:

(1) As a monomer for polymerization, (I) could be expected to display considerable reactivity. Not only is the olefinic bond activated by the carbonyl group, but the strained four-membered ring is highly susceptible to opening. Anionic polymerization could thus be

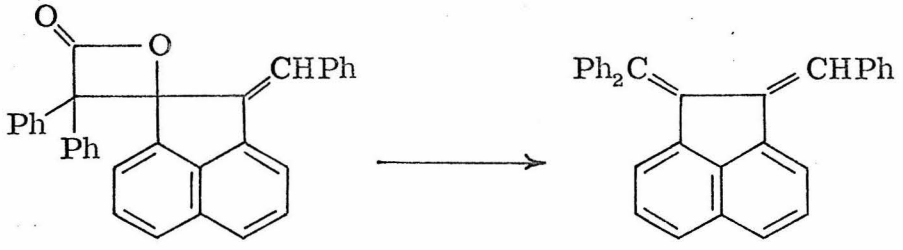
accomplished by two different, and quite likely, concurrent processes:



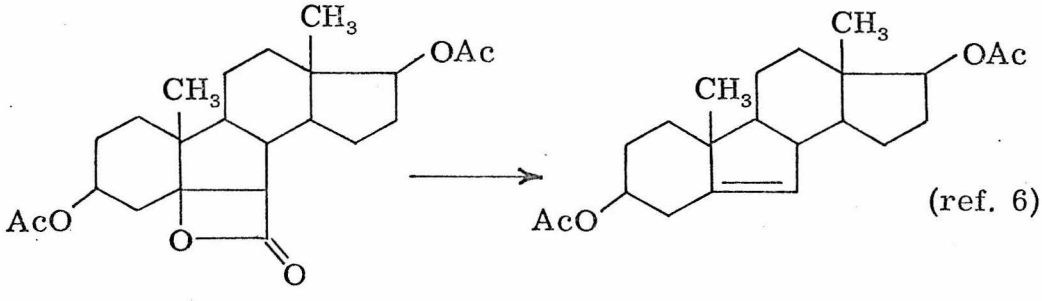
(2) Recently, it has been suggested that mass spectrometry might provide an important tool for predicting and interpreting photochemical reactions (2). When benzylcyclopropane, for example, is photolyzed in the vapor state, ethylene is formed in what is believed to be a unimolecular decomposition of an excited state. This process, as Turro points out, corresponds nicely to the metastable peak at m/e 82 in the low voltage mass spectrum of benzylcyclopropane. The photochemical type-II rearrangement of methyl alkyl ketones has an analogy in the mass spectrometer since only those ketones with γ-hydrogens give acetone photochemically and also give a peak at m/e 58 in the spectrometer. The rationale behind these correlations is that at low voltages the excited states produced by electron bombardment may be crudely similar to the excited states produced photochemically. Details of the decomposition paths might then be similar.

It is proposed that thiolactone (I) would be an interesting compound to use to test the goodness of mass spectrometric --

photochemical correlations, particularly since the photochemistry of (I) would be interesting in its own right. Photolysis of β-lactones does not seem to have been studied extensively. Noyes found that photolysis of liquid β-propiolactone gives a mixture of carbon monoxide, carbon dioxide, ethylene, acetaldehyde and polymer (3). The lactone thus behaved partly like a cyclic ketone and partly like an acid anhydride. In the case of (I), one intriguing path of photochemical fragmentation might be one in which allene and carbon oxysulfide are formed. It is known that relief of ring strain is an important factor in promoting efficient photodecarbonylation of cyclic ketones (4). This factor might also be important in promoting efficient photodethiocarboxylation. It is also known that in some cases β-lactones can lose carbon dioxide thermally. Two examples from the recent literature (5, 6) are shown below.



(ref. 5)



(ref. 6)

Two potential synthetic routes are now proposed for the preparation of α-methylene-β-propiothiolactone.

Both syntheses start with ethyl (α-hydroxymethyl)-acrylate, which is commercially available. Treatment with 48% HBr should give α-bromomethylacrylic acid. Treatment of this in step 2 of the first outline with benzoyl chloride (7) followed by reaction with trityl mercaptan at room temperature should give the trityl ester (8). In order to continue the sequence of reactions, this sensitive ester is first added to anthracene. The use of anthracene as a blocking agent is not new as it has been used by Roberts and Applequist in their synthesis of 3-methylenecyclobutanecarboxylic acid (9) and also more spectacularly by Bloomfield in his synthesis of diacrylylmethane (10). Acid hydrolysis of esters of trityl mercaptan is known to proceed with S-alkyl cleavage (11). In step 6 of the first outline, treatment of the thioacid with silver oxide is expected to lead to the β-thiolactone since an alkyl halide reacts much faster with a salt in which the metal is joined to a sulfur atom than with the corresponding oxygen compound (12). An analogous reaction is a common method of preparing β-lactones (13).

Steps 2-4 of the second outline illustrate the most common laboratory way of preparing mercaptans (14). Addition of α-mercaptomethylacrylic acid to anthracene and dehydration with dicyclohexylcarbodiimide (15) should produce the adduct (IX). Both synthetic sequences conclude with the reverse pyrolytic Diels-Alder reaction. Anthracene adducts seem to pyrolyze under milder

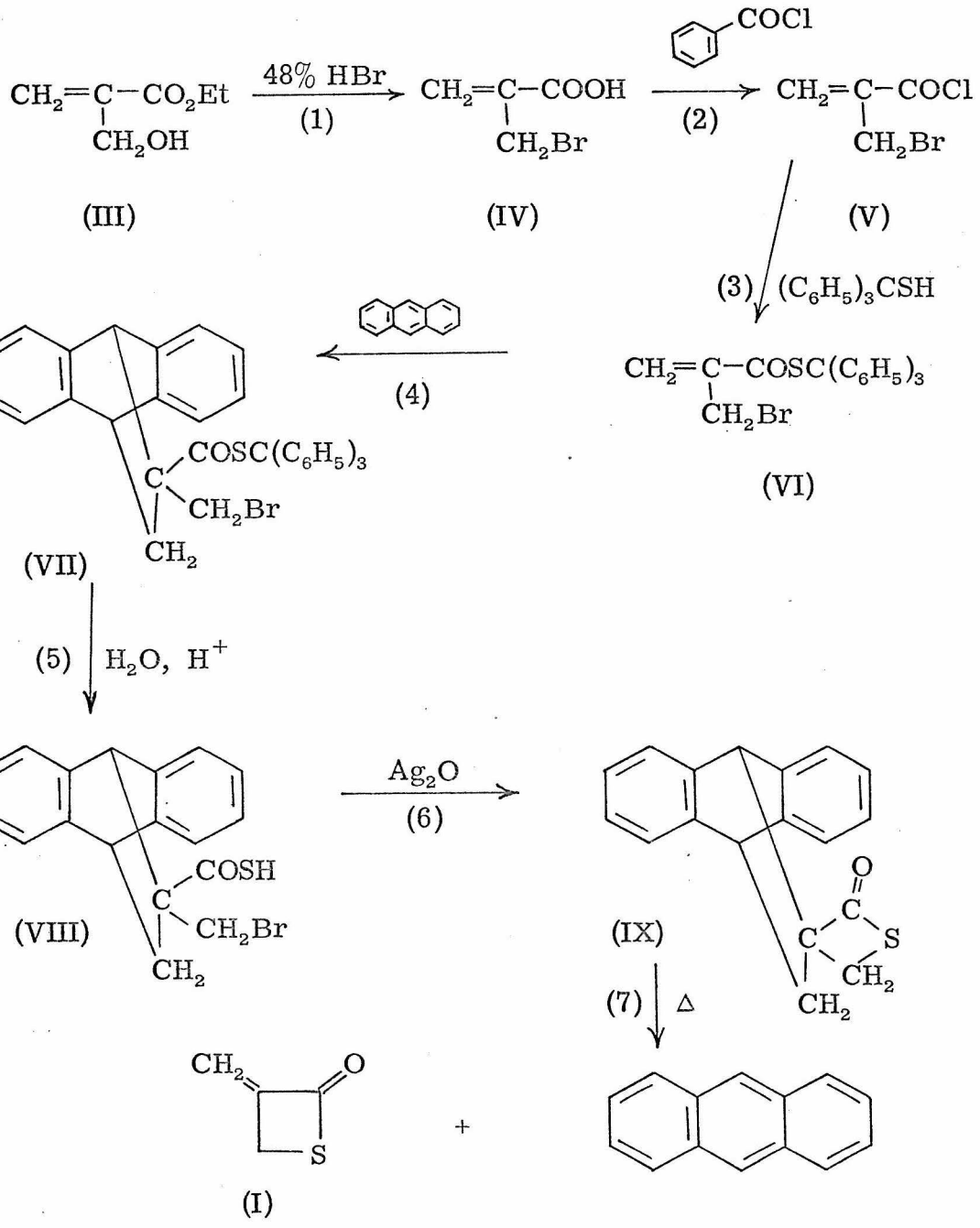


Figure 1. Outline 1 for the synthesis of α-methylene-β-propiothiolactone

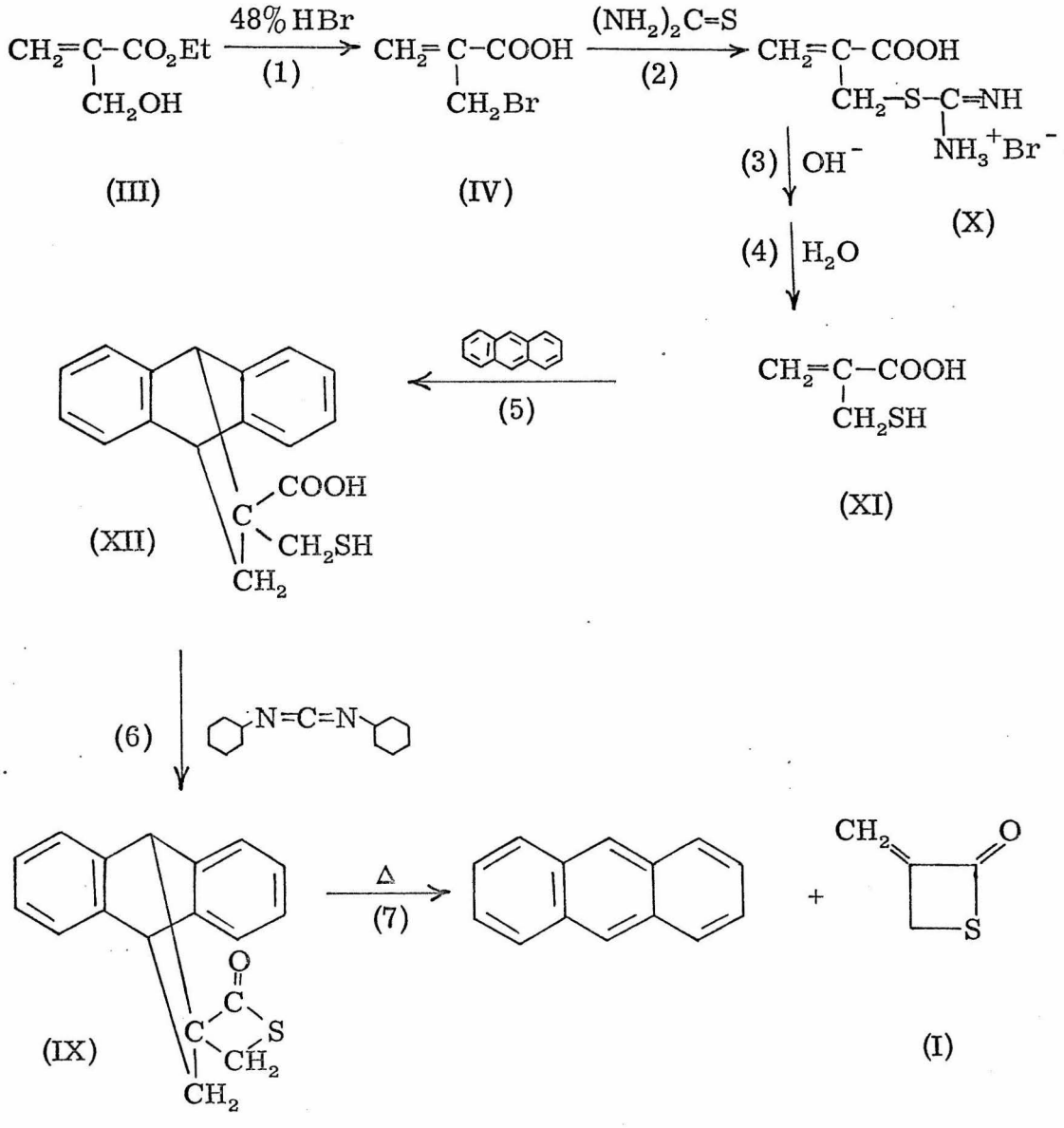


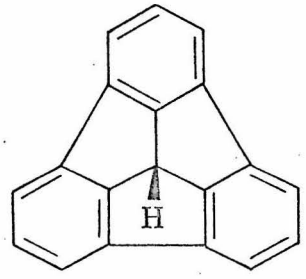
Figure 2. Outline 2 for the synthesis of α-methylene-β-propiothiolactone

conditions than other adducts (such as, for example, cyclopentadiene adducts), and typical reaction conditions for this step might be those employed by Bloomfield (10): pyrolysis of a mixture of (IX) and p-terphenyl at 20-30 mm under nitrogen and at a temperature of 125-150°.

Part B.

The preparation and the study of the properties of strained hydrocarbons is currently one of the very active fields of research interest. The majority of these hydrocarbons are small, non-aromatic compounds; in contrast, the [2.2]paracyclophanes become highly interesting on account of the presence of warped aromatic rings (16-18).

Compound (XIII), below, should have several interesting properties. The carbon skeleton of this molecule will not be planar because of the tetrahedral-like nature of the central carbon atom. However,



(XIII)

a model of (XIII) suggests that there will be considerable strain in the

molecule arising from distortions of the normal valence angles. It is proposed that in (XIII) the benzene rings will be distorted from planarity, and that this warping will be detectable in an X-ray analysis of the crystalline material.

The hydrogen on the central carbon should be acidic since it is formally a benzylic hydrogen with respect to three benzene rings. Streitwieser has suggested that acidity in planar unsaturated hydrocarbons is proportional to the difference in π-delocalization energy between the carbanion and the parent hydrocarbon (19). This correlation might not be expected to hold in the present case because of the nonplanarity of the parent material. On the other hand, it is a reasonable hypothesis that the greater the 2s-character of a carbon-hydrogen bond, the stronger the carbon acid. The plot below of percent 2s-character vs estimated pK_a is essentially linear (20).

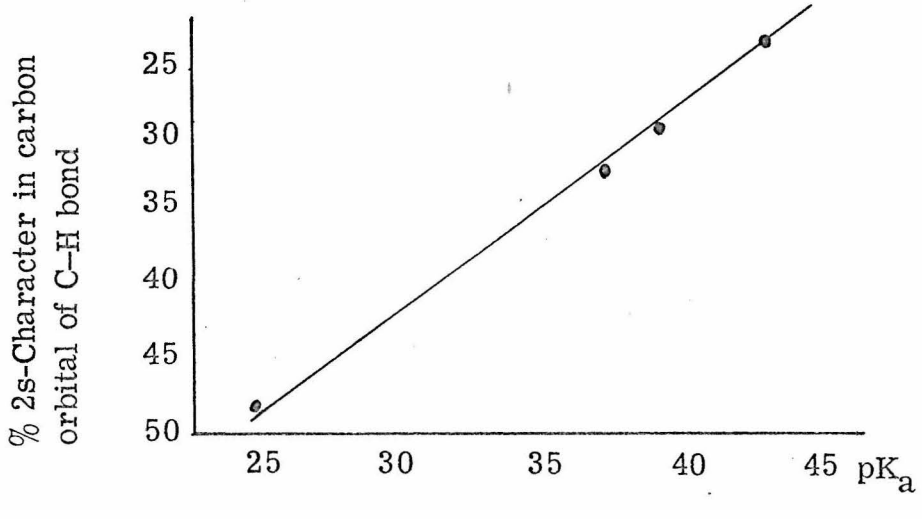


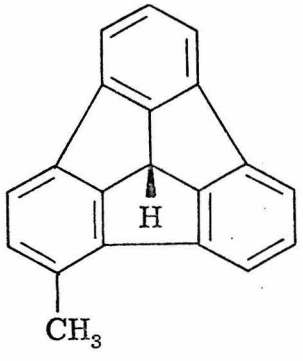
Figure 3. Plot of 2s-character vs estimated pK_a

Clearly, one would like to predict the pK_a of (XIII) in advance of experiment. To do this it would be necessary to know the precise geometry of the molecule, and in principle, this could be estimated by consideration of the factors of resonance energy, bond-stretching energy, and bond-angle-bending energy. Instead, we shall assume that the geometry has already been determined and that the CCC bond angles about the central carbon atom are known. These angles will be equal by symmetry, so that the central carbon atom must form three identical hybrid orbitals. If these are assumed to be of the form $\psi = \phi_{2s} + \sqrt{n}\,\phi_{2p}$, then orthonormality requires that $1 + n \cos\theta = 0$, where θ is the angle between two hybrid orbitals (21). The interpretation of n is that $\frac{n}{n+1}$ is the fractional amount of p-character in the hybrid orbital. Hence, $\theta = \sec^{-1}(-n)$ between two equivalent hybrids of the form sp^n. The percent 2s-character in the remaining fourth carbon atom (the one used to bond the acidic proton in (XIII)) is therefore

$$\%\,2s = \frac{100(n-2)}{n+1}$$

and it follows that from $\angle\theta$, one can ultimately obtain an estimate of the pK_a of (XIII).

An interesting effect occurs when a methyl group (or any other group) is substituted at certain places in (XIII); consider the derivative whose structure is shown below.



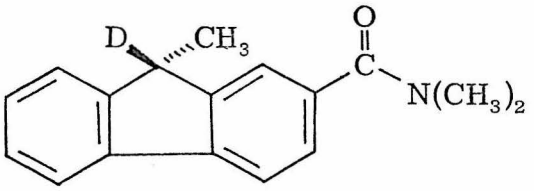
(XIV)

This compound should be capable of existing in two enantiomeric forms, since the skeleton is held in a rigid, nonplanar position. We may now pose the question of what happens to optically active (XIV) when the hydrocarbon undergoes ionization followed by reprotonation. Cram has developed a technique of studying carbanion stereochemistry by comparing the rates of base-catalyzed racemization and of hydrogen isotope exchange. If k_{ex} is the rate constant for exchange and k_r is the rate constant for racemization, four limiting cases are possible:

$k_{ex}/k_r \gg 1$		100% retention
$k_{ex}/k_r = 1$		100% racemization
$k_{ex}/k_r = 0.5$		100% inversion
$k_{ex}/k_r = 0$		100% isoracemization

Thus, in the base-catalyzed hydrogen isotope exchange of optically

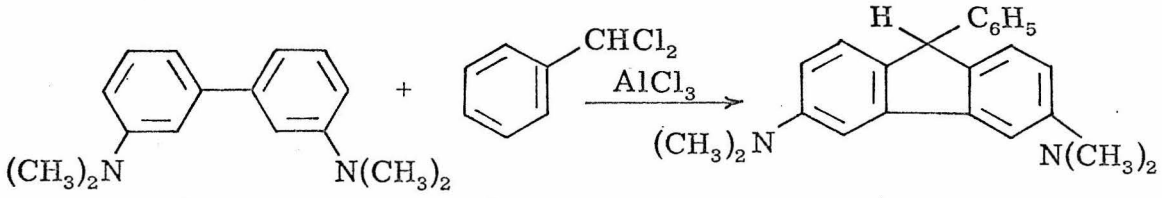
active (XV), k_{ex}/k_r was found to be greater than unity, indicating a retention mechanism (22).



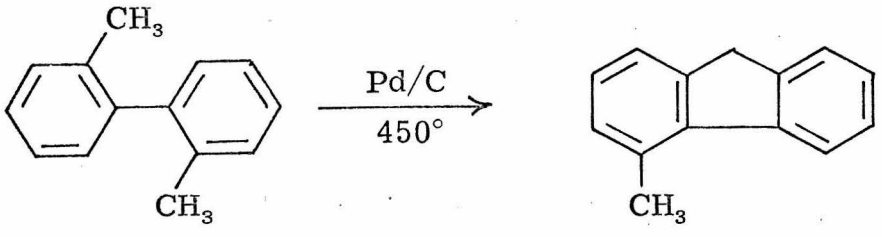
(XV)

It is proposed that the barrier to inversion of the carbanion of (XIV) through a planar configuration is so high (at moderate temperatures), that a retention mechanism will obtain.

A synthesis of (XIV) involves preparation of a suitable, 4,9-disubstituted fluorene. One route would be to carry out a Pschorr synthesis (23) on an appropriate o-aminobenzophenone or o-amino-diphenylmethane. Rieveschl and Ray point out that many fluorene derivatives have been made by carrying out a Friedel-Crafts reaction between a biphenyl and a gem-dichloro compound (24).

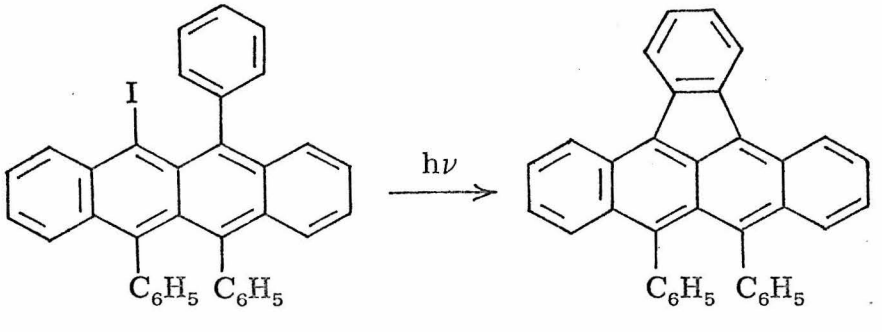


High-temperature dehydrogenation of certain biphenyl derivatives also leads to fluorenes (25).



These methods suffer from lack of generality or give low yields. A better mode of synthesis involves the dehydration of o-carboxydiphenyl derivatives, which was used successfully by Miller and Bachman in their syntheses of the 3- and 4-bromofluorenones (26).

The complete synthesis of compound (XIV), shown in Figure 4, features in the last step a photochemical ring closure. Kharasch has studied extensively the photolysis of iodoaromatic compounds (27); the first intramolecular cyclization to be effected in this manner was, in fact, a reaction leading to formation of a five-membered ring (28).



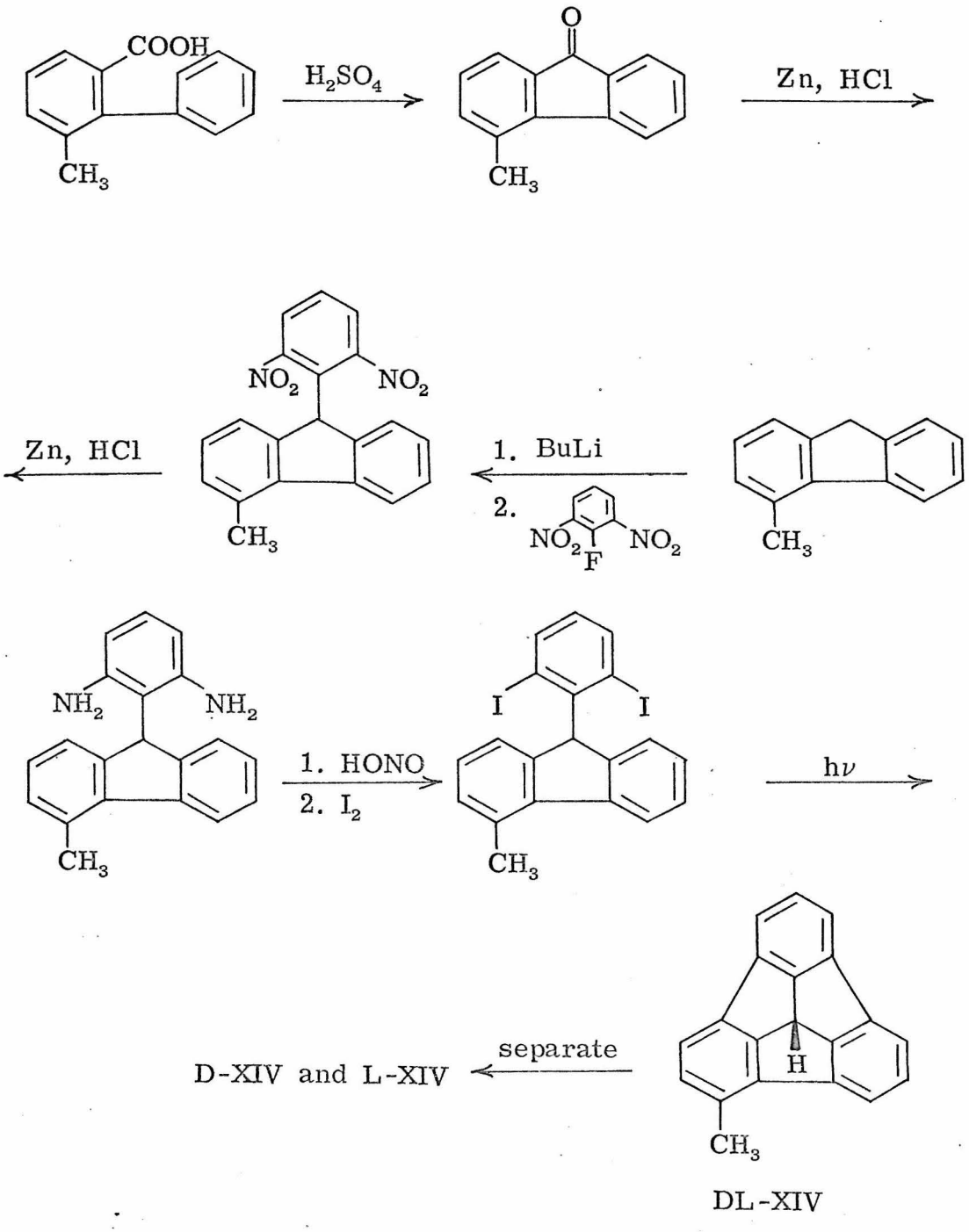
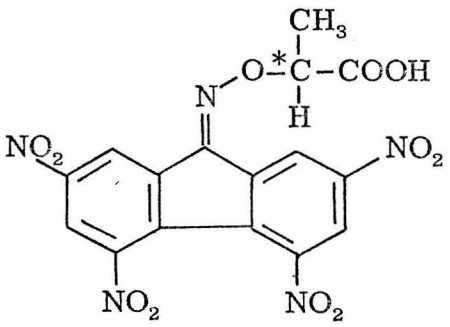


Figure 4. Synthesis of optically active (XIV)

Since the hydrocarbon product obtained from the synthesis will be a DL-racemate, some means of separation must be found in order that the base-catalyzed racemization can be studied. Newman and Lednicer resolved DL-hexahelicene by forming a charge-transfer complex with optically active (XVI), and then fractionally crystallyzing one of the two hydrocarbon enantiomorphs (29).



(XVI)

This procedure might be applicable to the present situation.

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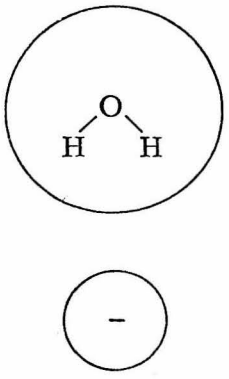
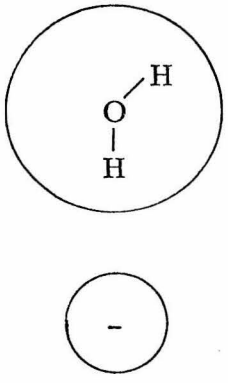
Proposition 2

Abstract. It is proposed that the Frank model for solvation of an ion be examined by computation using a potential function that contains ion-dipole, dipole-dipole, ion-induced dipole, dispersion and repulsions terms.

Traditionally, the solvation of ions has been treated as a purely electrostatic interaction of a charge and solvent multipoles. This type of treatment has limited applications, and further, several rather dubious assumptions must usually be made. For example, in considering the orientation of a solvating water molecule about an anion, Buckingham (1) favored structure (I), whereas Eley and Evans (2) preferred structure (II). Some authors have employed discontinuous models of solvation (3), while others have used continuous models (4, 5, 6).



(I)



(II)

These difficulties can be removed by making the model for solvation partly quantum mechanical in nature (7). For a particular ion assume an integral number of solvent molecules to comprise the primary solvation shell. In principle, the number of solvent molecules contained in a sphere of radius R with the ion at the center can be obtained from the ion-solvent radial distribution function (8), but nobody yet knows how to obtain such a function for a situation as complex as the present case (9).

Next, it is assumed that the potential energy of the system (ion plus first solvent shell) can be adequately represented by taking account of the major electrostatic interactions and of the intermolecular repulsions which exist for all molecules. Sposito and Babcock (7) considered the case of solvation of an ion by only one dipole, and included in their potential function just three terms:

$$\begin{aligned} U &= \text{ion-dipole} + \text{ion-induced dipole} + \text{repulsion} \\ &= -\frac{q\mu}{r^2}\cos\theta - \frac{q^2\alpha}{2r^4} + Br^{-12} \end{aligned} \tag{1}$$

However, a rough calculation shows that for the general case where n dipoles surround an ion, dipole-dipole and dispersion terms can also become important. Thus, to apply quantum mechanics to this situation would be similar in nature to solving the Schrodinger equation for the many-electron atom (10), where the potential function now is

$$U = \text{ion-dipole} + \text{dipole-dipole} + \text{ion-induced dipole} + \text{dispersion} + \text{repulsion}$$

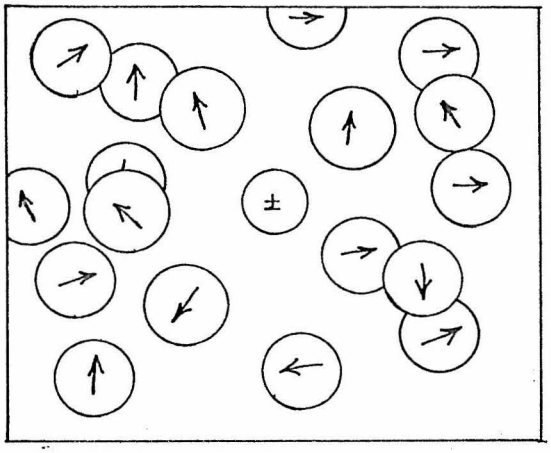
$$= -\sum_{i=1}^{n} \frac{q\mu_i}{r_i^2} \cos\theta_i - \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} \frac{\mu_i \mu_j}{r_{ij}^3} [g(\theta_i, \theta_j, \phi_i, \phi_j)]$$

$$- \sum_{i=1}^{n} \frac{q^2 \alpha_i}{2 r_i^4} - \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} \frac{3}{2}\left(\frac{h\nu_i h\nu_j}{h\nu_i + h\nu_j}\right) \frac{\alpha_i \alpha_j}{r_{ij}^6} + \sum_{i=1}^{n} \frac{B}{r_i^{12}}$$

$$+ \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} \frac{C}{r_{ij}^{12}} \qquad (2)$$

One method of approach would thus be to apply the procedure of the self-consistent field, which was pioneered by Hartree (11). From the total "electronic energies" so obtained, one can construct the partition function for the system and thence calculate any desired thermodynamic property.

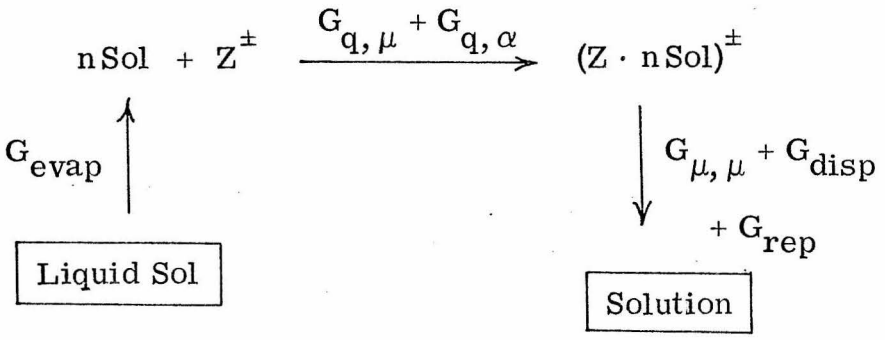
This method has the advantage that it does not assume at the offset any preconceived configuration of dipoles about the ion. However, it is likely to run into the same difficulty faced by all SCF calculations, namely computational laboriousness. The advent of high-speed computers makes it possible to return to equation (2) and perform a classical, electrostatic treatment that is economically feasible. Consider a system (see III, below) composed of an ion and n dipoles in a certain configuration at time t = 0. The potential energy of the system is next computed according to equation (2), and



(III)

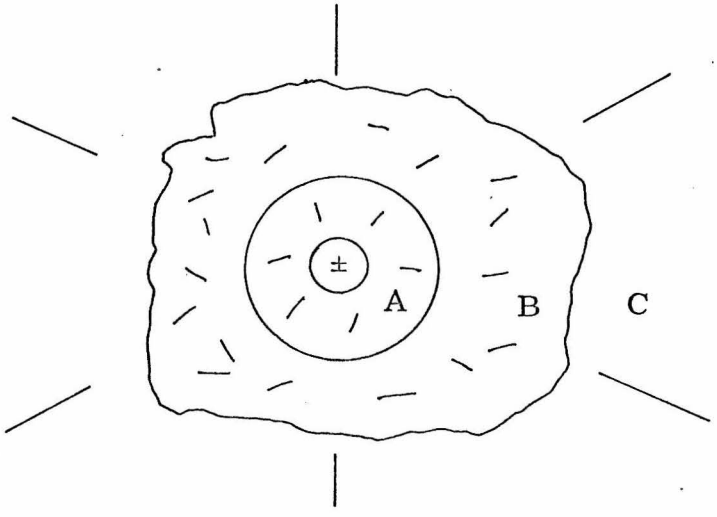
in general, this energy will not be the minimum energy available to the system. To achieve this we begin moving the dipoles systematically about the ion, computing the potential energy after each move. If a move increases U, we reverse the move and execute a different one. An algorithm would have to be developed for handling all the particles in an ordered manner. Boundary conditions need not be imposed on the system since the maximum in energy can only occur when all the dipoles lie at infinity. A convenient number of dipoles which can be treated in this way is 100. When the preferred configuration is reached, the final potential energy is computed.

A Born-Haber cycle for solvation is shown below (Sol represents solvent). Hence, the free energy of solvation is simply



$$\Delta G_{solv} = G_{evap} + U. \qquad (3)$$

The inclusion of a large number of solvent dipoles in the computational scheme allows one to investigate an effect postulated by Frank and Wen (12). According to the picture sketched by these workers (see IV, below), the solvent about an ion consists of three regions: a region of immobilization (A), a region of moderate structure-breaking (B), and a region of "normal" solvent (C).



(IV)

The relative sizes of regions A and B are assumed to be a function of the size and charge of the ion; thus, for a sufficiently large ion, the magnitude of the field may be reduced to such an extent that region A will be negligible. Gurney (13) believes this has happened for I^-($R \sim 2.16$ Å). The cause of the structure-breaking in region B is presumably the balance which exists between the force due to the spherically symmetrical ionic field and the orienting force of neighboring water molecules.

Nobody has any idea of the approximate magnitude of the B region for a given ion. Region A is frequently assumed to consist of essentially a single sheath of solvent molecules (4-10, usually), and it is possible that region B may not be a significantly more populous area than the A region. It is proposed that the Monte Carlo calculation just outlined be carried out for the case of the lithium ion in an attempt to get computational evidence for the existence of the B region. In order to characterize the amount of order in a given shell, we may examine the orientation of each dipole relative to a line joining its center to the center of the ion. In terms of the conventional spherical polar coordinates, complete order in a shell may be defined by the conditions:

$$r = \text{same value for all dipoles}$$
$$\theta = 180°$$
$$\phi = 0°$$

A simple function which can be used to roughly describe the order is shown below:

$$g = \frac{1}{n}\sum_{i=1}^{n}\left[\left(\frac{r_i - \bar{r}}{r_{max}}\right)^2 e^{-(r_i-\bar{r})^2/r_{max}^2} + (\cos\theta_i + 1)^2 e^{-(\cos\theta_i + 1)^2} + (\cos\phi_i - 1)^2 e^{-(\cos\phi_i - 1)^2}\right] \quad (4)$$

This function is zero when the above conditions are satisfied, and is otherwise non-negative.

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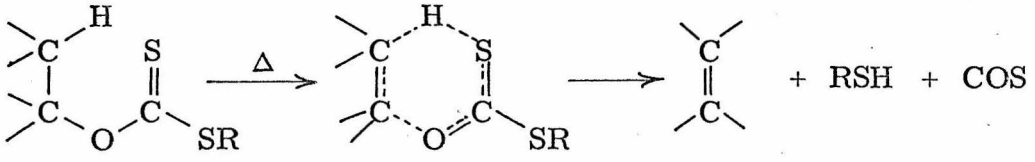
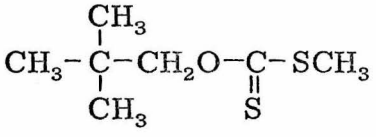
Proposition 3

Abstract. Some experiments are proposed in order to elucidate the mechanism of the pyrolysis of certain xanthates. Some of these lack β-hydrogen atoms, yet they have been reported to give olefinic products.

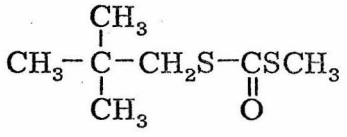
It has been accepted since the time of the work by Barton (1) and by Cram (2) that the Chugaev reaction is a completely concerted, cis-elimination, in which it is the thion sulfur atom which attacks the β-hydrogen atom.



It is interesting to inquire what would happen if there were no β-hydrogen atoms available. The pyrolysis of methylneopentyl xanthate (I) would seem to be typical, for this substance yields the more stable dithiocarbonate (II) in good yield (3). Methyl-2, 2, 6, 6-tetramethylcyclohexyl xanthate behaves similarly.

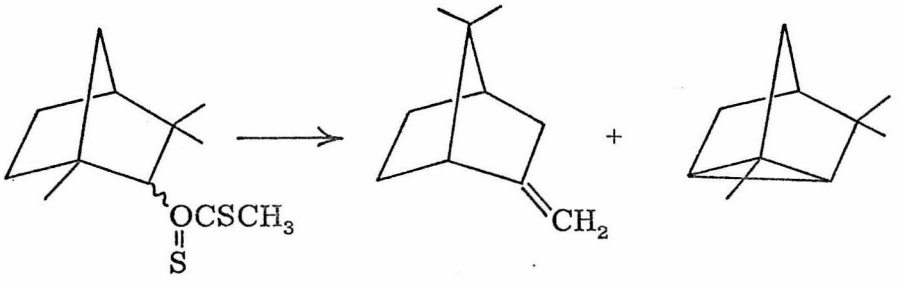


(I)



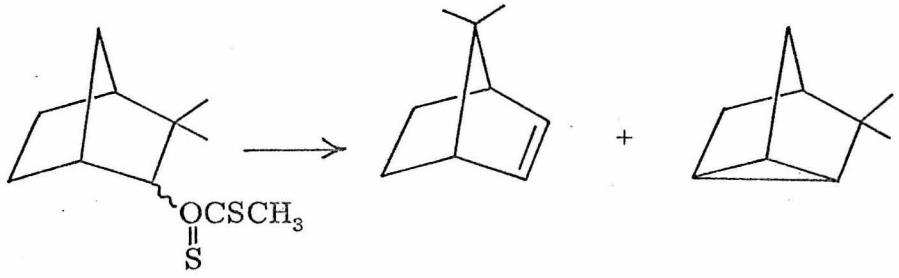
(II)

There exist, however, a few examples in the literature in which such behavior is not observed. Several investigators (4a-c) found that when methylfenchyl xanthate (III, stereochemistry unknown) was pyrolyzed, there was obtained α-fenchene (IV) and cyclofenchene (V); one group obtained approximately equal amounts of the two hydrocarbons (4c).



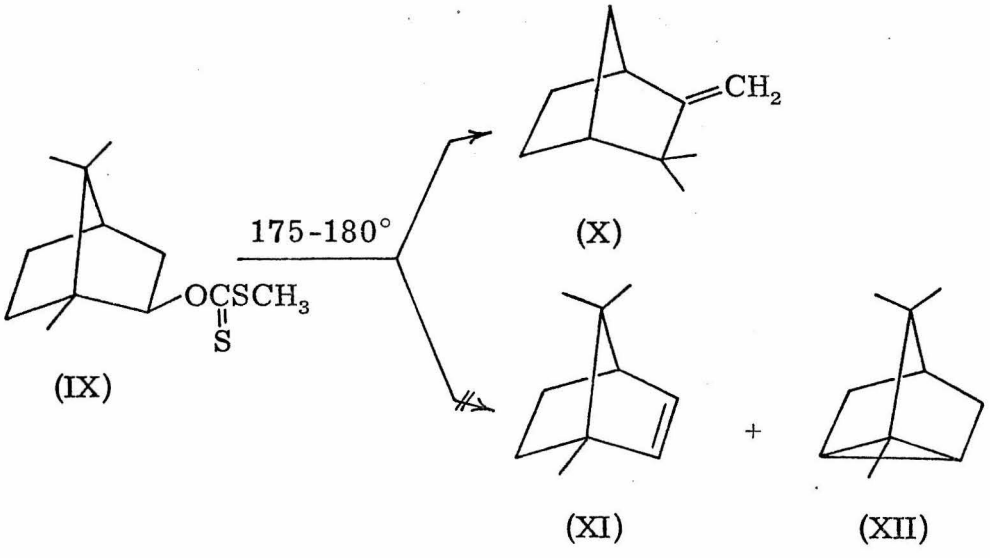
(III) (IV) (V)

In methylcamphenilyl xanthate (VI) there is only one β-hydrogen atom, but Bredt's rule prohibits its removal in an olefin-forming process. Nevertheless, on pyrolysis (VI) was reported (5) to yield apobornylene (VII) and apocyclene (VIII).

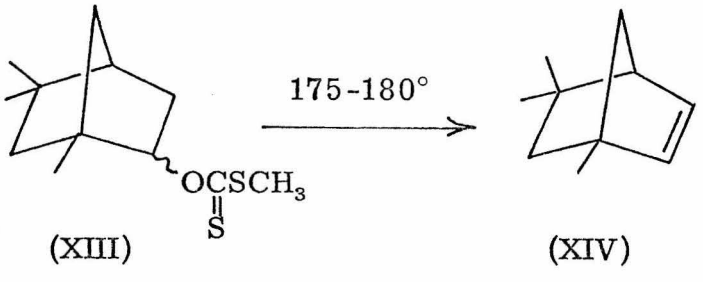


(VI) (VII) (VIII)

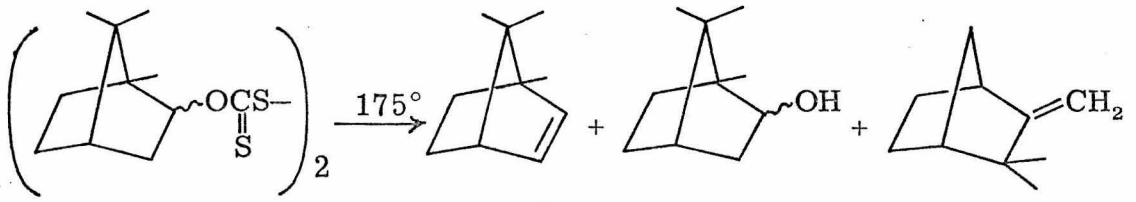
A more striking rearrangement is one reported by Hückel (6), who found that when methylisobornyl xanthate (IX) was pyrolyzed, the hydrocarbon product was essentially all camphene (X); he did not rule out the possibility that traces of bornylene or tricyclene could also have been present.



This result seems to be in contrast to that obtained by Qvist (4c) and by Nametkin (7), who found that methyl-α-isofenchyl xanthate (XIII) produces only the normal product isofenchylene (XIV).

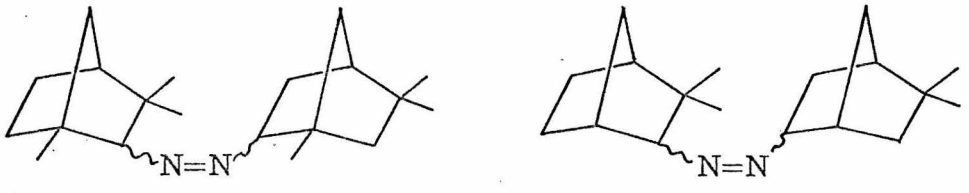


Finally, in one case where a dixanthide was pyrolyzed, some rearranged product (camphene, X) was obtained (8).



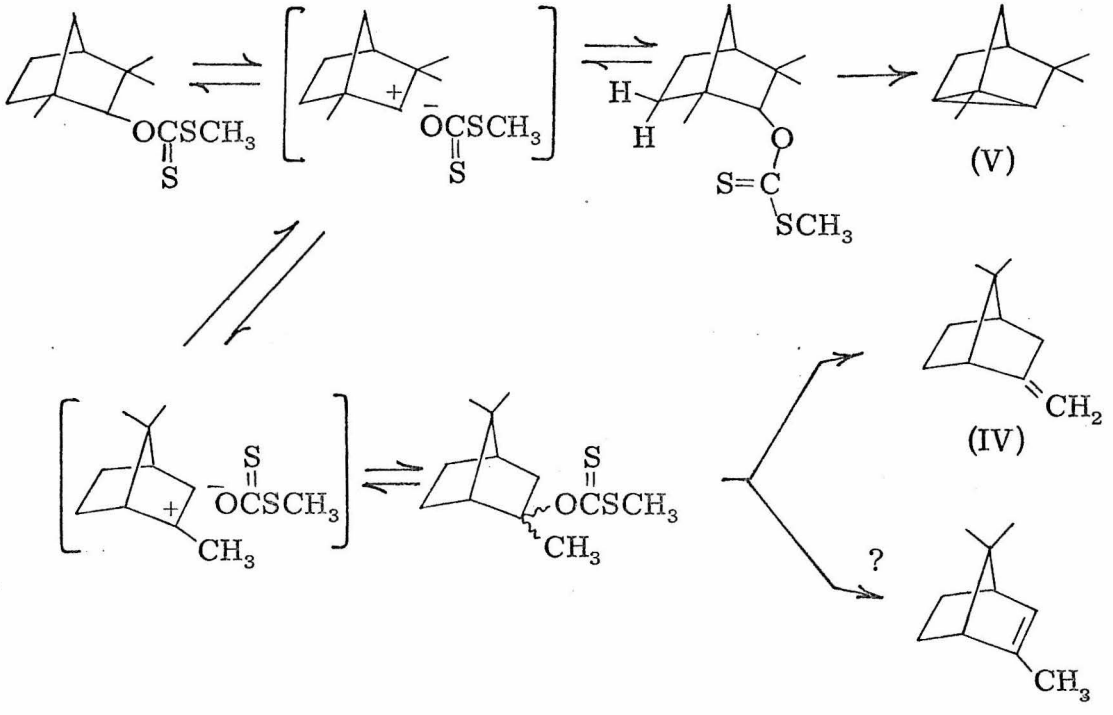
(XV) (XI) (XVI) (X)

In summary, these examples suggest that in certain instances the "molecular mechanism" pathway of Barton's has been superseded, in part or in whole, by another pathway. The recent work by Berson on the Wagner-Meerwein rearrangement of the 2-bornyl radical offers the possibility that a radical pathway might be operating in the above examples (9a, b, c). If the results of Hückel are indeed correct, however, the radical pathway for this particular example is probably not correct since Berson failed to detect any camphene when he generated the 2-bornyl radical (9c). This conclusion is rendered suspect, though, by the difference in reaction conditions under which the two experiments were performed. It would be interesting to have product data for the pyrolyses of 2-azofenchane (XVII) and 2-azocamphenilane (XVIII).

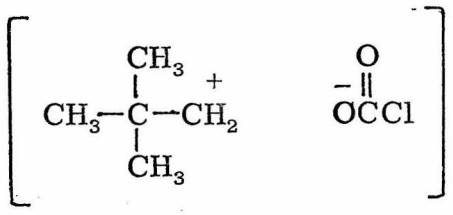


(XVII) (XVIII)

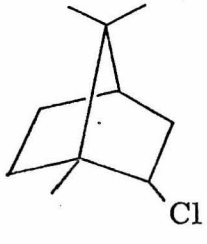
A reinvestigation of the pyrolysis of the xanthates mentioned earlier would seem desirable. At least two conceivable explanations of these results are possible. It may be that in these systems we are observing further examples of Wagner-Meerwein rearrangements of radicals. It is also possible that the rearrangements are proceeding through ion pairs. The case of methylfenchyl xanthate, assuming an exo-configuration, is illustrated below:



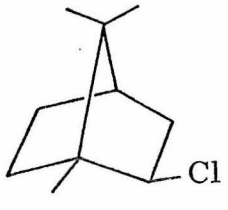
This mechanism is similar to that proposed by Lewis and Herndon for the pyrolysis of certain chloroformates (10). These authors suggested that the ion pair shown below is an intermediate in the formation of neopentyl chloride, 2-methyl-1-*butene and*



2-methyl-2-butene from neopentyl chloroformate. Later, Maccoll and Swinbourne (11) found that the gas-phase pyrolysis of neopentyl chloride at 444° gives an equilibrium mixture of methylbutenes. No induction period was evident, addition of propene did not affect the reaction, and a Wagner-Meerwein rearrangement of a "quasi-heterolytic" species was postulated. Bicknell found that the pyrolysis of bornyl (XIX) and isobornyl chlorides (XX) gives some rearranged products (12). The major product from the former is tricyclene (XII, 55%) and from the latter camphene (X, 75%). These pyrolyses also quite likely proceed via an ion-pair pathway.



(XIX)



(XX)

It is proposed that an accurate product analysis be made of the pyrolysis of xanthates (III), (VI) and (IX) in order to establish the structures of all the hydrocarbon products formed. Stability of the olefinic products under the reaction conditions would have to be investigated. To distinguish between a radical or an ion-pair pathway, the

following experiments would be useful:

(1) If a radical pathway of some kind is involved, the rate of the reaction should be affected by carrying out the pyrolyses in an oxygen-rich atmosphere, or in an atmosphere containing propene or nitric oxide.

(2) An all-radical pathway could be examined by pyrolyzing the analogous azo compounds under identical conditions and examining the resulting product composition.

(3) A determination of the entropy of activation for the formation of the products would give some indication of the amount of cyclic character in the transition state. Typically, multicenter-type reactions such as the Cope and Claisen rearrangements have entropies of activation in the neighborhood of -10 eu.

(4) As a rule, reactions in which charge is generated in the transition state proceed faster in solvents of increasing dielectric constant. If the ion-pair mechanism be correct, then it is expected that the rate of reaction should vary accordingly when several eliminations are carried out in solvents of different dielectric constant. Prior measurement of the dielectric constant of the solvent at high temperature would have to be made since such data would probably not be available for materials of interest (13).

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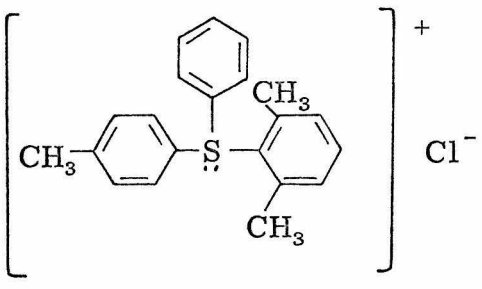
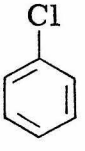
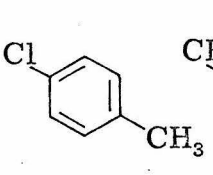
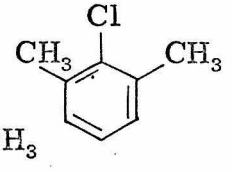
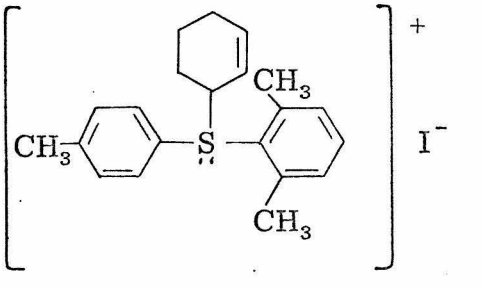
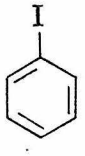
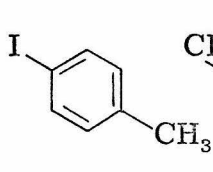
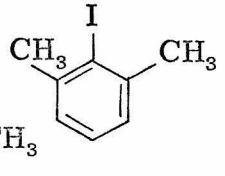
Proposition 4

Abstract. A prediction is made concerning the behavior of the iodide salts of certain group VI "onium" derivatives upon hydrolysis; this prediction relates to a hypothesized tetracovalent intermediate in the hydrolyses.

The "onium" compounds of the chalcogens represent a complete set of closely related compounds within which it should be possible to test proposed correlations or predictions. A systematic study of these compounds with such views in mind does not seem to have been done. Sulfonium salts have been the most extensively studied, the two most frequently studied reactions that they undergo being solvolysis and pyrolysis. Although it is known that selenonium and telluronium salts pyrolyze in a manner similar to that of the sulfur analogs (1), the exact degree of similarity is not known.

Wiegand and McEwen have recently reported some interesting results on the thermolysis of triarylsulfonium halides (2). A portion of their data is reproduced in the table below. In the opinion of these authors, the product ratios are consistent with neither an aromatic S_N1 nor an S_N2 mechanism. On a purely statistical basis one is apt to rule out the S_N1 mechanism since there is only one authenticated case of a set of reactions which proceed by an aromatic S_N1 mechanism. Therefore, because in the above pyrolyses it is the least electrophilic carbon which appears to undergo attack, it was suggested

Table 1. Pyrolysis of Two Triarylsulfonium Halides at 250°

Halide	Molar ratio of aryl halides		
	 1.50	 1.00	 5.00
	 3.30	 1.00	 15.7

that the mechanism operating is actually the transient formation of a tetracovalent intermediate which preferentially decomposes so as to relieve strain arising from nonbonded repulsions (in this case, the interactions with the methyl groups at the 2- and 5-positions of one of the benzene rings).

Several comments can be made concerning this proposed mechanism. First, the tetracovalent intermediate seems to have been invoked solely in connection with the strain element. The thermolysis

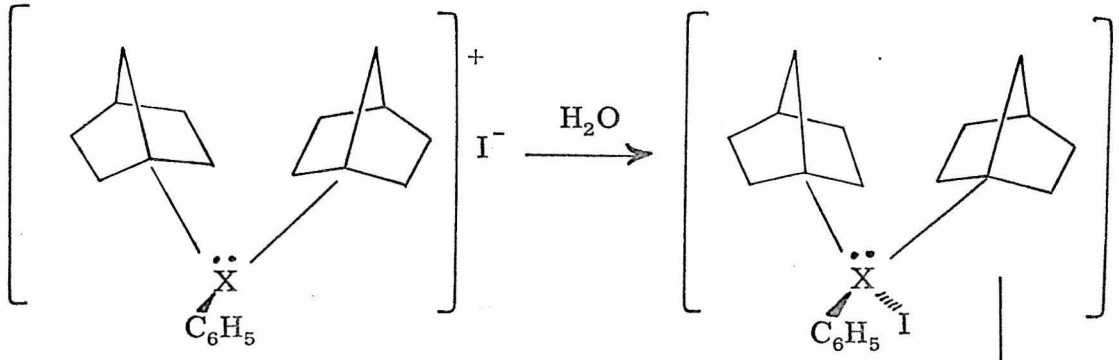
of diphenyl-p-tolylsulfonium bromide produces bromobenzene and p-tolyl bromide in a molar ratio greater than two, but it is not clear that the authors wish to retain the same mechanism for this case. Second, it is not clear that the usual directive influences observed in aromatic S_N2 reactions should necessarily be followed in a molten mixture; the structure of melts is one of the major problems in the field of fluid studies. Third, Wiegand and McEwen suggest no specifics concerning the actual decomposition of the tetracovalent intermediate.

It is proposed that the concept of a tetracovalent intermediate, however, has merit in its own right. From tables of atomic energy levels it is found that the energy required to promote an electron from the valence np level to the (n+1)s level is 211, 151, 138 and 125 kcal for oxygen to tellurium, respectively (3). Thus, oxygen should be least likely to form a fourth covalent bond, whereas tellurium should have the greatest proclivity to do so. The facts bear this out; no tetracoordinate oxygen compounds are known, whereas sulfur, selenium and tellurium form a host of such compounds. The formation of tetraphenyltellurium (4) and tetraphenylpolonium (5) has recently been reported.

$C_6H_5SF_3$ $\qquad$ $(CH_3\overset{\overset{O}{\|}}{C}CH_2)_2SeCl_2$ $\qquad$ $(CH_3)_2TeI_2$

In view of the remarks made earlier, it seems best to look for evidence of the intermediacy of a tetracovalent chalcogenide in a system where major questions concerning the structure of the

medium do not have to be considered and where the problem of relief of strain has been minimized. In addition, one has to have a means of discerning whether or not attack has occurred on the central atom. It is assumed that once the tetracovalent intermediate is formed, it will decompose essentially indiscriminately to give a statistical distribution of products. Accordingly, it is proposed that the decomposition of salts of the general structure (I) in aqueous solution (6) is a more reasonable reaction in which to look for evidence of the formation of an intermediate (II).



(I)

(X = S, Se, Te)

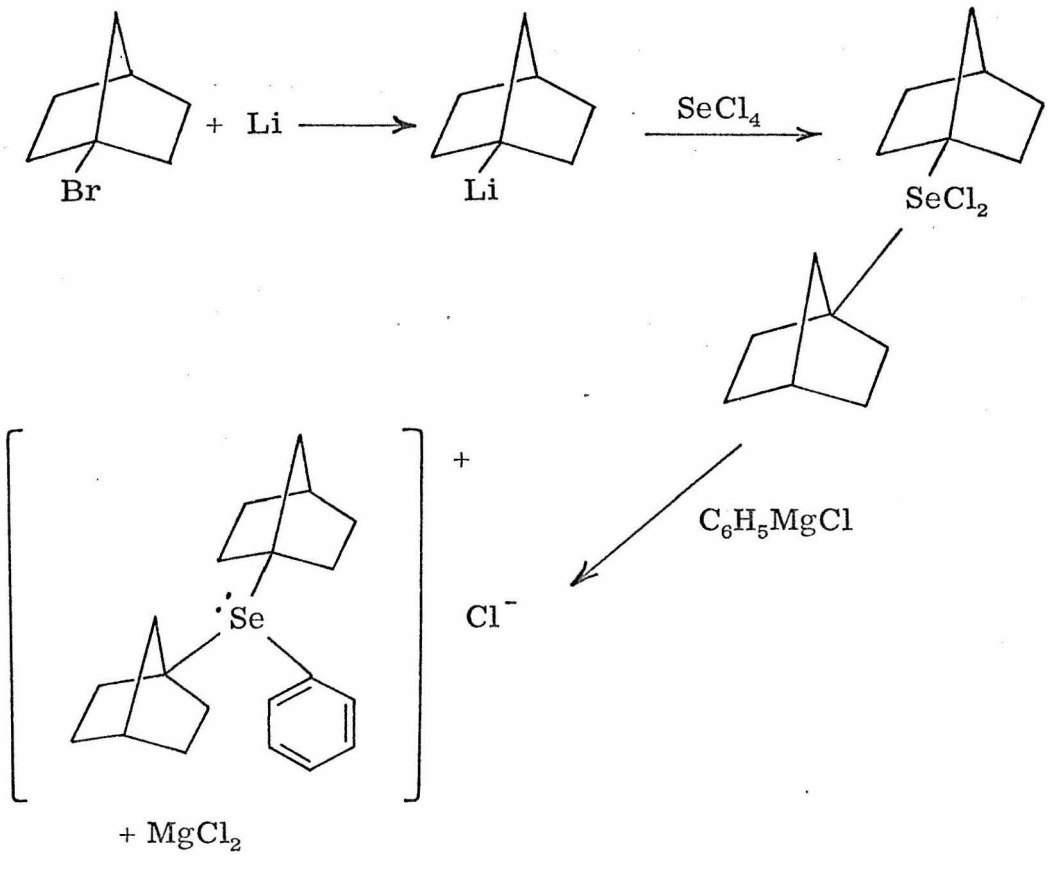
(II)

products

The estimated atomic polarizabilities of sulfur, selenium and tellurium in their +1 oxidation states are 4.0, 19.2 and 79 $Å^3$, respectively (7). Thus, as far as these centers are concerned, the sequence sulfur-selenium-tellurium is in the order of increasing softness (as an acid), and hence, from the principle of hard and soft

acids and bases, the greatest chance for binding should occur when the base is also soft (8). Iodide ion is the softest of the halide ions. No contribution to an S_N2 attack can come from reaction at the 1-norbornyl center, so that the isolation of any 1-iodonorbornane implies the formation of a tetracovalent intermediate which has subsequently decomposed homolytically. The molar ratio of 1-iodonorbornane to iodobenzene should increase along the sequence S-Se-Te.

General methods for the preparation of sulfonium salts include treatment of a sulfide with an alkyl halide, addition of a Grignard reagent to a sulfoxide (9), reaction of a diarylalkoxysulfonium salt with an aryl Grignard reagent (10), and so on. Generally, methods that are suitable for preparing sulfonium salts are also suitable for preparing selenonium and telluronium salts. For the most part, however, these methods depend on reactions which could not be expected to occur at the 1-position of the norbornane ring. Reactions of Grignard reagents with chalcogens or their halides generally prove disappointing (11); a better method is suggested by the work of Winstein and Traylor (12) on the preparation of organic, bridgehead mercurials. For selenium or tellurium the following synthetic route is suggested (and illustrated with the case of selenium):



Reaction of the organolithium with $SeCl_4$ (or $TeCl_4$) may stop at the selenide (or telluride) stage; however, a general reaction of the latter is their addition with halogens.

For the preparation of the desired sulfonium salt, it is expected that 1-norbornyllithium will react with thionyl chloride to produce the sulfoxide; treatment of this with phenylmagnesium iodide in the usual way will give the sulfonium salt (13).

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6. Use of this medium minimizes any chance that the reaction will proceed through ion pairs, which may be implicated in solvents of dielectric constant less than 25: J. B. Hyne, Can. J. Chem., 39, 1207 (1961); J. B. Hyne and J. W. Abrell, ibid., 39, 1657 (1961); J. B. Hyne and J. H. Jensen, ibid., 40, 1394 (1962).

7. Calculated from the approximate expression $\alpha = \frac{4a_o^3}{9n}\left[\sum_{j=1}^{n} \overline{r_j^2}\right]^2$, where n is the number of electrons, and the averages of the squares of the distances are computed with the aid of Slater's rules; see the paper by J. G. Kirkwood in R. H. Cole (ed.), "Dielectrics -- Intermolecular Forces -- Optical Rotation," Gordon and Breach, New York, 1965, p. 181.

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Proposition 5

Abstract. A simplified method is proposed for estimating the extent of nonplanarity of hexahelicene. The method is first examined by performing a calculation on a simpler system, biphenyl.

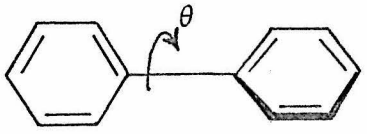
Hexahelicene is an interesting substance because of the helicity which it possesses; presumably, it is this structural feature which is responsible for the extremely high optical rotation of $\pm 3640°$ (1). The recently synthesized heptahelicene, octahelicene and nonahelicene also have very large values of the optical rotation (2, 3).

Hexahelicene is prevented from being planar by intramolecular overcrowding, but an X-ray analysis of the substance has not yet been reported. It is here proposed that an estimate of the nonplanarity of hexahelicene can be obtained by considering the balance between the energies of two opposing interactions: the resonance energy or π-electron delocalization energy of the system, which will be a maximum when the system is planar, and the energy arising from nonbonded repulsions of proximate atoms. It is recognized that other effects may contribute, such as bond stretchings and bond-angle bendings (4-7). At the present level of approximation, these will be considered subordinate to the other two effects.

In order to test the validity of the method on a specific case, calculations were carried out on biphenyl. An X-ray analysis of

biphenyl gives the length of the middle bond as 1.48 Å (8), which is essentially the value expected for an sp^2-sp^2 C–C single bond (9). Biphenyl has previously been treated by molecular orbital methods (10).

In simple, molecular orbital terms two quantities vary with the angle of twist θ, the resonance integral and the overlap integral.



The variable resonance integral is calculated from the Mulliken formula (11)

$$\beta = \beta_0 \frac{S(1+S)}{S_0/(1+S_0)} \qquad (1)$$

where the subscript zero refers to biphenyl when the angle of twist is 0°. From the tables of Kopineck (12) the overlap integral S_0 is found to have a value of 0.24 when R = 1.48 Å. The new overlap integral is then obtained by the simple formula (13).

$$S = S_0 \cos\theta. \qquad (2)$$

Combining equations (1) and (2) we get

$$\beta = \frac{1.24 \cos\theta}{1 + 0.24 \cos\theta} \quad (\text{in units of } \beta_0) \qquad (3)$$

To calculate the nonbonded repulsion energy we need suitable potential functions. Bartell has proposed some rather hard potential functions (14); his hydrogen-hydrogen function has the form shown below. This function, together with the carbon-hydrogen and

$$V_{HH} = 6600 \exp(-4.08\ r) - 49.6\ r^{-6} \qquad (4)$$

r is in Å

V is in kcal/mole

carbon-carbon functions of Bartell's, were used by Gleicher and Schleyer in their recent, successful treatment of strain in bridgehead carbonium ions (15).

A harder hydrogen-hydrogen function is one investigated by Simmons upon following up a suggestion of Mulliken's. This function is of the form (16)

$$V_{HH} = AIS^2/2(1-S^2) \qquad (5)$$

A is a constant

I is ionization potential of hydrogen in ev

S is H–H overlap integral

Simmons found that a good value of A for hydrocarbons is 0.95. Converting to kcal/mole we have

$$V_{HH} = 149\ S^2\ (1-S^2)^{-1} \qquad (6)$$

The overlap integral may be approximated by the exact expression for the overlap of two isolated hydrogen atoms:

$$S = e^{-R}(1 + R + \tfrac{1}{3}R^2) \qquad (7)$$

R is in au

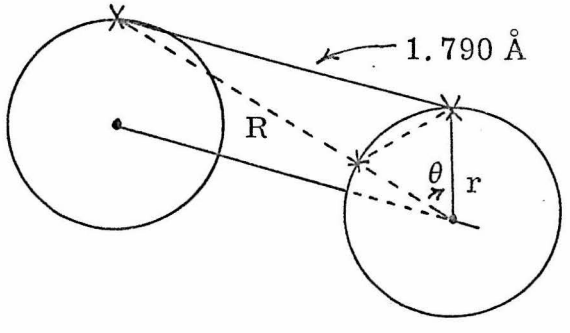
In the table below is a comparison of equations (4) and (6) for various values of R; the last column also gives values computed from an expression (similar to equation (4)) which was obtained by fitting the parameters to lattice data for crystalline, aromatic hydrocarbons (17).

Table 1. Comparison of Nonbonded Repulsion Energies Calculated from Several Potential Functions

R (Å)	Equation (4)	Equation (6)	Williams
1.00	61.94	91.32	59.20
1.50	10.16	27.02	11.47
1.790	2.98	13.04	3.87
2.00	1.13	7.40	1.72
2.50	0.043	2.06	0.181
3.00	-0.036	0.533	0.005
3.520	-0.022	0.123	-0.011
4.00	-0.012	0.031	-0.008
5.00	-0.003	0.002	-0.002

Equation (6) is seen to be purely repulsive in nature and at least four times harder for all values of R of interest. A few sample calculations sufficed to show that when repulsion energies calculated from equation (6) were combined with the corresponding resonance energies, the energy of the system steadily decreased from 0 to 90°.

Using standard values for the carbon–carbon and carbon–hydrogen bond lengths in biphenyl, one can show that for the planar situation the cis, ortho hydrogen atoms are 1.790 Å apart. When biphenyl is not planar, the H–H distance may be computed as follows:



Each cis hydrogen is considered a point on a circle; one circle remains at rest while the other rotates θ degrees. The radius of the rotating wheel is easily found to be 2.148 Å . Hence, for a given angle of twist the H–H distance is

$$R_{HH} = \sqrt{(1.790)^2 + [\,2(2.148)\sin\frac{\theta}{2}\,]^2} \qquad (8)$$

$$= 3.038\sqrt{1.347 - \cos\theta}$$

Calculations were carried out for 13 different orientations. The results are given in Table 2, and the total energies are plotted versus the angle of twist in Figure 1.

Table 2. Energy Calculation on Biphenyl Rotamers

Angle	Distance (Å)[a]	NBE[b] (kcal/mole)	RE[c] (kcal/mole)	Sum (kcal/mole)
0°	1.790	5.96	-6.89	-0.93
20	1.940	3.02	-6.26	-3.24
23	1.982	2.46	-6.06	-3.60
26	2.030	1.96	-5.83	-3.87
30	2.105	1.48	-5.49	-4.01
33	2.163	0.99	-5.22	-4.23
36	2.225	0.62	-4.91	-4.29
39	2.305	0.44	-4.61	-4.17
42	2.360	0.30	-4.28	-3.98
45	2.430	0.16	-3.94	-3.78
48	2.500	0.09	-3.59	-3.50
70	3.045	-0.07	-1.10	-1.03
90	3.520	-0.04	-0.00	-0.04

[a] Distance between two cis, ortho hydrogens.

[b] Nonbonded repulsion energy, composed of two equivalent interactions, and computed from equation (4).

[c] π-Delocalization energy.

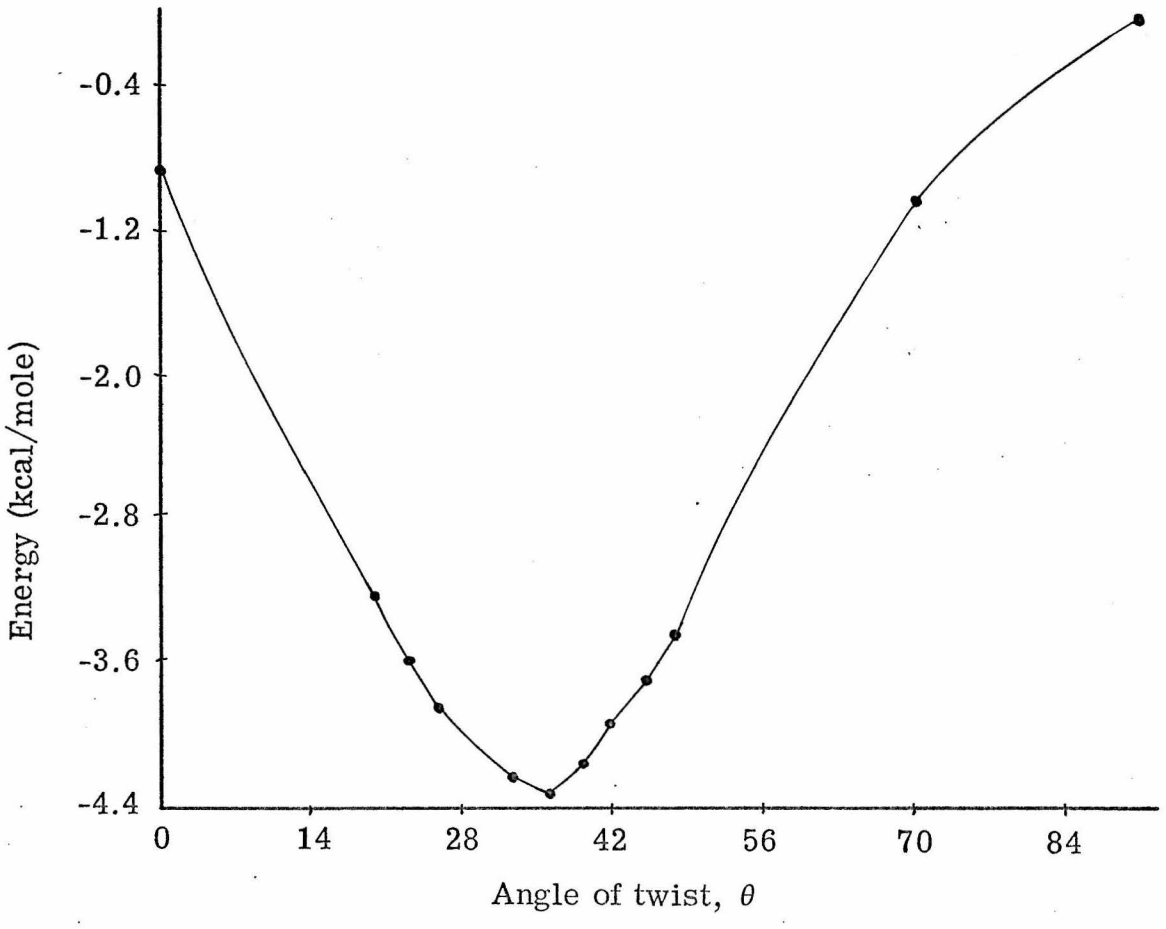
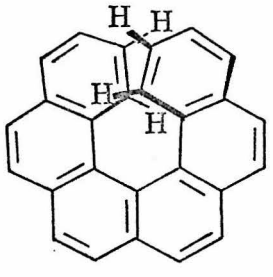


Figure 1. Plot of energy vs angle of twist in biphenyl

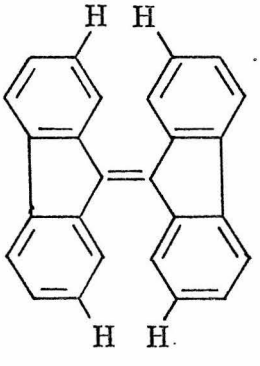
The results show that a preferred conformation exists at about 36-37°. A recent X-ray measurement by Bastiansen's group gives a value of 41.6° as the preferred angle of orientation (18). Considering the approximations that have been made, the agreement is satisfactory.

To summarize, for biphenyl it has been found that consideration of just two factors, nonbonded repulsion and π-delocalization, lead to

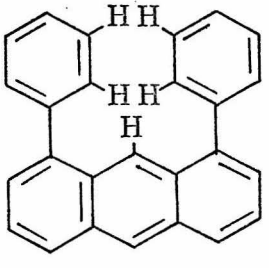
a satisfactory model for the structure. By hypothesis, similar considerations should apply to other aromatic molecules such as hexahelicene (I), and the interesting molecules (II) and (III). Inclusion of additional repulsions (carbon-hydrogen and carbon-carbon) may be necessary in these situations. Parenthetically, it might be added that



(I)



(II)



(III)

the success of this method would allow one to estimate nonbonded potential parameters for other atoms with a minimum of effort. Thus, by working backward from known structures of various fluorinated hydrocarbons, one should be able to deduce a reasonable set of fluorine potential functions.

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BIOGRAPHY

I, Joseph B. Dence, was born in Toledo, Ohio on December 16, 1941, of Joseph B. and Jayne C. Dence. Schooling at the elementary level was obtained at Mt. Vernon Grade School and after graduation in 1955, there followed one year of secondary schooling at Woodward High School. I was graduated from Rogers High School in Toledo in 1959 as valedictorian of my class, and in the fall of that year entered Cornell University in Ithaca, New York. In February of 1960 I transferred to Bowling Green State University in Bowling Green, Ohio, and obtained a B. A. degree from there in June, 1963 (3. 71/4. 00). After spending a summer at E. I. DuPont de Nemours, Inc. in Wilmington, Delaware, I entered graduate school in the fall of 1963 at the California Institute of Technology in Pasadena, California. The year 1964-1965 was spent on a leave of absence.